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Kyoto University
Homoeptoc octahedral coordination of CH_{3}CN to Mg^{2+} in the Mg[N(SO_{2}CF_{2})_{2}]_{2}-CH_{3}CN system

Gleb Veryasov, Kazuhiro Matsumoto and Rika Hagiwara

X-ray diffraction and Raman spectroscopic measurements revealed a homoeptoc octahedral coordination of CH_{3}CN to Mg^{2+} in the [Mg(CH_{3}CN)]_{2}(TFSA)_{2} (TFSA = bis(trifluoromethylsulfonyl)amide) crystal structure and in Mg(TFSA)_{2}/CH_{3}CN electrolytes.

In addition to improving the commonly used Li-ion batteries, novel batteries are being developed for future applications, especially in large-scale energy devices.\(^1\) Magnesium secondary batteries comprising a magnesium metal negative electrode have higher energy density, improved safety, and lower cost than lithium secondary batteries. Thus, since the report of the first practical cell in 2000 by Aurbach et al.,\(^2\) they have been considered as attractive candidates for various purposes.\(^2,4,5\)

The main challenges in the development of Mg secondary batteries are related to the design of new cathodes and electrolytes.\(^3,6\) To date, the most popular electrolytes still lack the necessary requirements to produce a viable product. Ethereal solutions of RMgX, MgAlCl_{2}R_{2}, and Mg(AlCl_{3}R')_{2} (R and R' = alkyl or allyl groups) are widely used because they enable stable Mg metal deposition/dissolution behavior.\(^2,5,7\) In addition, magnesium–aluminum chloride complexes provide a wide electrochemical window within the anodic limit of Mg deposition–dissolution.\(^3\) The Mg source Mg(TFSA)_{2} (TFSA = bis(trifluoromethylsulfonyl)amide) readily dissolves in polar solvents and its Mg^{2+} ions have high affinity to $\sigma$-donor ligands.\(^6\) Its acetonitrile (AN) solution has been examined by several research groups as an electrolyte for Mg secondary batteries.\(^3,6\) In 2012, Tran and co-workers investigated in details the use of Mg(TFSA)_{2}/AN electrolyte for magnesium secondary batteries.\(^6\) Although the Mg(TFSA)_{2}/AN electrolyte is not suitable for reversible Mg deposition, its high oxidative stability indicated its potential use as an alternative to Grignard-based electrolytes.\(^6\) The solution structure plays an important role in electrode reactions and diffusion processes in batteries. However, to the best of our knowledge, there are no experimental reports on the structure of the Mg(TFSA)_{2}/AN electrolyte; the only computational work by Rajput et al.\(^9\) was devoted to the investigation of ion pair formation in Mg-based electrolytes. In the present study, we succeeded in isolating high-quality crystals of [Mg(AN)]_{2}(TFSA)_{2}, which were analyzed

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1 Electronic Supplementary Information (ESI) available: Experimental details; Detailed information on X-ray structure determination (Table S1-S2) and Raman spectra recording; Details on D–H–A interactions in [Mg(AN)]_{2}(TFSA); (Fig. S1, Table S3); Packing diagram of [Mg(AN)]_{2}(TFSA); (Fig. S2); List of bands observed in the Raman spectrum of [Mg(AN)]_{2}(TFSA); (Table S4); Raman spectrum of Mg(TFSA)_{2} powder (Fig. S3, Table S5); Raman spectrum of the liquid obtained after [Mg(AN)]_{2}(TFSA); crystal melting (Fig. S4); Full-scan Raman spectra of pure acetonitrile and Mg(TFSA)_{2}–acetonitrile solutions (Fig. S5); Raman spectra of pure acetonitrile, Mg(TFSA)_{2}–acetonitrile solutions, and [Mg(AN)]_{2}(TFSA); region between 100 and 800 cm\(^{-1}\) (Fig. S6). The CIF file for [Mg(AN)]_{2}(TFSA); can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, CCDC 1437045. See DOI: 10.1039/40xx00000x

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**Fig. 1** ORTEP diagram of the [Mg(AN)]_{2}(TFSA); complex. Thermal ellipsoids are drawn at 50% probability. Symmetry operations: (i) 1-x, y, z; (ii) 1-x, y, 1-z. Bond length and angles: Mg1–N41 2.1477(12) Å, Mg1–N61 2.1439(12) Å, Mg1–N81 2.1549(12) Å, N41–Mg1–N61 89.11(5)°, N41–Mg1–N81 90.33(4)°, N61–Mg1–N81 89.81(5)°.\(^{10,11}\)
by X-ray diffraction. Raman spectra of this compound and of Mg[Tf2SO]x-acetonitrile solutions provided detailed insights into the structural properties of Mg[Tf2SO]2/AN electrolytes.

Single crystals of [Mg(AN)x][Tf2SO]x were grown by fast removal of acetonitrile under dynamic vacuum upon contact of acetonitrile with Mg[Tf2SO]x (see ESI† for more details). The [Mg(AN)x][Tf2SO]x crystals easily melt at about room temperature (~30 °C); after melting, the compound does not recrystallize. It should be noted that complete dissolution of Mg[Tf2SO]x in acetonitrile resulted in a transparent homogeneous solution, without any evidence of crystal formation. The obtained [Mg(AN)x][Tf2SO]x was extremely hygroscopic and rapidly deliquesced in air. Exposure to air for 2 days resulted in the formation of crystalline materials composed of [Mg(H2O)x][Tf2SO]y, as confirmed by X-ray crystallography.10,11 Inclusion of solvents into a crystal lattice was also observed for some alkali and alkaline earth metal salts.10,12

[Mg(AN)x][Tf2SO]x crystallizes in the P21/n space group with the following parameters: a = 8.8749(5) Å, b = 15.2823(8) Å, c = 12.9264(7) Å, and β = 104.8572° (2). The ORTEP diagram of the [Mg(AN)x][Tf2SO]x complex is shown in Fig. 1. Details of crystal data collection and refinement and selected geometric parameters are given in Tables S1 and S2, ESI†. In the coordination sphere of Mg2+, three crystallographically independent anion molecules form a homoleptic octahedral environment by a crystallographic inversion operation. The Mg(AN)x moiety is surrounded by eight Tf2SO anions and each anion forms weak C–H···O interactions with acetonitrile molecules, with H···O distances varying from 2.50 Å to 2.67 Å (VdW radii are 1.20 Å for H and 1.52 Å for O); for more details, see Fig. S1 and Table S3, ESI†. These interactions contribute to the formation of a 3D network in which cations and anions are organized in 1D columns (see Fig. S2, ESI†).

The Tf2SO anions are known to adopt cis and trans conformations.14 In the structure of [Mg(AN)x][Tf2SO]x, these anions adopt a trans conformation, having roughly C2 symmetry, with C–S–N–S torsion angles of 109.27(11)° and 94.10(12)° for C1–S1–N1–S2 and C2–S2–N1–S1, respectively. The formation of Mg(AN)x21 has been previously observed in the structures of [Mg(AN)x][SbCl6]15 and [Mg(AN)x][Bi2Cl10]16. The Mg...N distances are 2.1439(12) Å, 2.1477(12) Å, and 2.1549(12) Å for the three crystallographically independent anion molecules and are comparable with those reported (2.1347(2)–2.179(8) Å) for [Mg(AN)x][SbCl6]15 and slightly shorter than those (2.20(2)–2.25(3) Å) observed in the structure of [Mg(AN)x][Bi2Cl10]16. The weak C–H...O interactions between acetonitrile molecules and Tf2SO anions may prevent crystallization from the completely dissolved acetonitrile solution of Mg[Tf2SO]2. Because the mixing of Mg[Tf2SO]x and acetonitrile in a 1:6 ratio led to the formation of Mg[AN]x2–[Tf2SO]x with homoleptic Mg[AN]x2–, higher levels of acetonitrile are expected to generate a similar Mg coordination sphere. Formation of [Mg(H2O)x][Tf2SO]y(H2O)z owing to the final water consumption process indicates that the Mg2+...O3– bond energy is higher than that of Mg2+...NCCH3, and even small amounts of water form strongly bonded hydrates.

The Raman spectrum of [Mg(AN)x][Tf2SO]x, shown in Fig. 2, was recorded on a single crystal, confirmed by X-ray diffraction and sealed in a 0.5 mm glass capillary under dry atmosphere (for details, see Table S4, ESI†). The assignments were made based on literature data17 and the Raman spectrum of pure Mg[Tf2SO]x powder was used for the identification of the Tf2SO anion band (see Fig. S3 and Table S5 ESI†). The characteristic frequency of coordination compounds containing acetonitrile is the C≡N stretching vibration, denoted as v(C≡N). In the spectrum of [Mg(AN)x][Tf2SO]x, three v(C≡N) bands at 2266, 2293, and 2318 cm−1 were detected. This splitting can be interpreted by considering normal coordinate analysis for octahedral species (A1g and E) and factor group splitting (lowering of symmetry from O6 to C3).18 In pure acetonitrile,19 this band appears at 2249 cm−1 and is expected to shift toward higher or lower frequencies depending on the nature of the moiety.20 In the IR spectrum of [Mg(AN)x][Bi2Cl12]23, v(C≡N) appeared as a doublet at 2322 and 2290 cm−1 for x = 2 and at 2320 and 2289 cm−1 for x = 3. The most intense band in the Mg[Tf2SO]2 and [Mg(AN)x][Tf2SO]x spectra corresponds to the combination of δ(CF3) and ν(SNS) vibrations (see assignments in Table S5, ESI†) at 754 and 748 cm−1, respectively. The position of this band related to Mg2+ was discussed by Watkins et al.21 (also in the case of Li+ by Umebayashi et al.22), its appearance at higher frequencies indicates a stronger bonding of the anion to the metal core. Because there is no Mg2+...Tf2SO contact in [Mg(AN)x][Tf2SO]x, the δ(CF3) + ν(SNS) band appears at a frequency that is 6 cm−1 lower than that of pure Mg[Tf2SO]2. According to previous reports, the ν(C≡N) and ω(Mg2+...NC) (ω = wagging) bands are supposed to appear at 340–350 cm−1 and 250–255 cm−1, respectively.23 The ω(Mg2+...NC) bands are too weak to be detected in the present spectrum; moreover, ν(Mg2+...N) overlaps with the t(SO3) (t = torsion) band at 338 cm−1 (see Fig. S3, ESI†).

The spectrum of the liquid obtained after [Mg(AN)x][Tf2SO]x crystal melting is shown in Fig. S4, ESI†. The three ν(C≡N)
stabilized by H···O interactions, which should appear together.

This is not observed in the Raman spectra of the liquid samples, and the band appears at 378 \( \text{cm}^{-1} \) for both 0.5 M and 1:10 solutions. This indicates that acetonitrile molecules are not immobilized by the C–H···O interactions with the TFSA\(^-\) anions because of the mobility of the TFSA\(^-\) anions in the liquid state.

The \( \nu(\text{Mg}--\text{O}) \) band was reported to appear at around 250 \( \text{cm}^{-1} \) in the Raman spectrum of the Mg(TFSA\(^-\))\(_2\)–[BMPyr][TFSA]\(^-\) (BMPyr = N-butyl-N-methylpyrrolidinium) liquid. This band was not observed in the spectrum of the acetonitrile solution of Mg(TFSA\(^-\))\(_2\) and presumably corresponds to the peak at 259 \( \text{cm}^{-1} \) in the spectrum of pure Mg(TFSA\(^-\))\(_2\) powder (see Fig. S3 and Table S5). The \( \delta(\text{CF}_3) + \nu(SNS) \) band (discussed above for pure Mg(TFSA\(^-\))\(_2\) powder and [Mg(AN)\(_6\)][TFSA\(_2\)] adduct) appeared at 741 \( \text{cm}^{-1} \) in the 1:10 solution and at 739 \( \text{cm}^{-1} \) in the 0.5 M solution. This supports the absence of bonding between the TFSA\(^-\) anions and Mg\(^{2+}\) ions in solution.

The results of this study show that, in acetonitrile solutions of Mg(TFSA\(^-\))\(_2\), Mg\(^{2+}\) is in a homoleptic octahedral coordination with acetonitrile molecules. Raman spectroscopy reveals the mobility of the TFSA\(^-\) anions, which adopt a trans conformation in both [Mg(AN)\(_6\)][TFSA\(_2\)] salt and...
Mg[TFSA]₂⁻–acetonitrile solutions. In a recent report, Rajput et al. performed a computational study of solvation in different Mg-based electrolytes, including the Mg[TFSA]₂⁻/AN system. Radial distribution functions for the cation–cation, cation–anion, and cation–solvent pairs obtained by molecular dynamics simulation allowed them to conclude that Mg²⁺–TFSA interaction is dominant compared with the Mg²⁺–acetonitrile interaction. However, our investigation strongly suggested that Mg²⁺ ions form an entity with six acetonitrile molecules and Mg²⁺–TFSA⁻ interaction does not occur.

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Notes and references