The First Structurally Characterized Aluminum Squaraine Complex: $L_2(AlMe_2)_4 \cdot 2THF \cdot 2$toluene [L = Bis(2,6-diisopropylanilino)squaraine]

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Dedicated to Professor Helmut Schwarz on the occasion of his 60th birthday

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Bis(2,6-diisopropylanilino)squaraine (**1**) was prepared by condensation of squaric acid and 2,6-diisopropylaniline. Treatment of **1** with trimethylaluminum affords a novel dimeric aluminum squaraine complex: $L_2(AlMe_2)_4 \cdot 2THF \cdot 2$toluene [L = bis(2,6-diisopropylanilino)squaraine] (**2**), which was characterized by X-ray diffraction.

Introduction

Squaraines are a class of 1,3-derivatives of squaric acid in which the substituents are amines or highly electron-donating aromatic or heterocyclic groups.[1] Their electronic structure and rich chemistry have been the subject of considerable discussion.[2] Several of them show fluorescence[3] or form self-organized films,[4] which imply their application as photosensitive films, organic solar cells, optical recording, and non-linear optical materials.[5] However, research on the organometallic chemistry of squaraines seems to be neglected. In fact, the versatility of squaraines implies that this class of compounds are ideal ligands. Only a few diamino derivatives of squaric acid have been structurally characterized.[2b,2c,6] No complex of aluminum with squaraines as ligand has been isolated and structurally characterized so far. We became interested in employing diaminosquaraines as ligands with the aim of studying their novel structure and property. Herein, we report on the first aluminum complex with the squaraine ligand.

Results and Discussion

Diamino derivatives of squaric acid can be synthesized as main products through the condensation of squaric acid with amines.[7] The ligand, bis(2,6-diisopropylanilino)squaraine (**1**) was prepared by a modified approach of refluxing squaric acid and 2,6-diisopropylaniline in ethanol with a few drops of formic acid as catalyst, as outlined in Scheme 1. The IR spectrum of **1** shows a strong absorption at 1598 cm^{-1} attributed to the squaraine carbonyl group.[2g] The 1,3-derivative of **1** is formed preferentially in this condensation reaction instead of the 1,2-species.[7b−7e] A sharp band at 3151 cm^{-1} is attributed to N−H stretching vibrations,[7b,7c] and a band at 2870 cm^{-1} to $\nu(N^+H)$.[7c] Ligand **1** is an air-stable solid which decomposes above 380 °C. The EI mass spectrum gives the molecular ion peak at $m/z = 432$ and the base peak at $[M^+ - C_3H_7]$. The composition of **1** is further supported by the ^1H and ^{13}C NMR spectra. However, an unambiguously structural assignment can only be made by an X-ray analysis. So far, we have not been able to grow suitable single crystals of **1**.

Bis(2,6-diisopropylanilino)squaraine (**1**) is sparingly soluble in most organic solvents. The reaction between trimethylaluminum and a suspension of **1** in THF was carried out at −78 °C. The acidic hydrogen of **1** is very active towards the CH_3 groups of trimethylaluminum. A clear yellow solution of **2** was readily formed upon warming to room temperature (Scheme 1). Complex **2** is much more soluble than **1** in organic solvents.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$. An overview and numbering scheme is shown in Figure 1. The aluminum squaraine complex **2** turns out to be an interesting dimer with two different coordination modes for Al atoms. Two squaraine moieties are linked together by two $AlMe_2$ units, forming a ten-membered $C_4Al_2N_2O_2$ ring. Two THF molecules coordinate to the Al atoms of the two exocyclic $AlMe_2$ units by O−Al coordinative bonds, whereas the two exocyclic $AlMe_2$ units are linked to the O atoms of the squaraines by Al−O covalent bonds. In the ten-membered $C_4Al_2N_2O_2$ ring each Al atom is surrounded by the O atom, N atom and two Me groups. The N(2) atom adopts an sp^2 electron distribution and the Al−N bonds are

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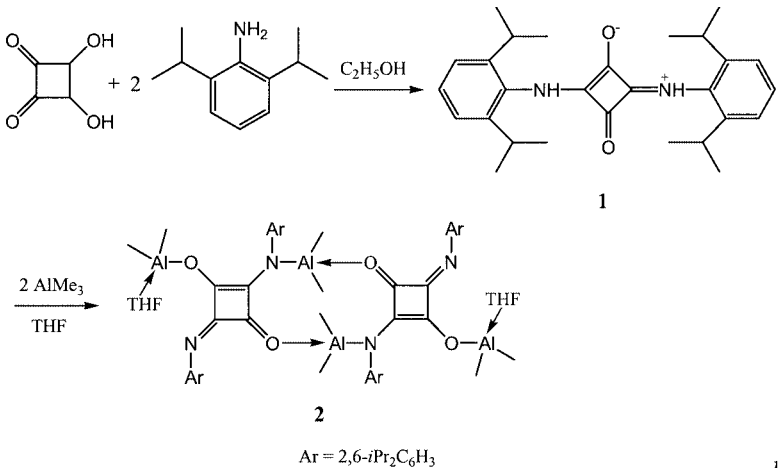

Scheme 1

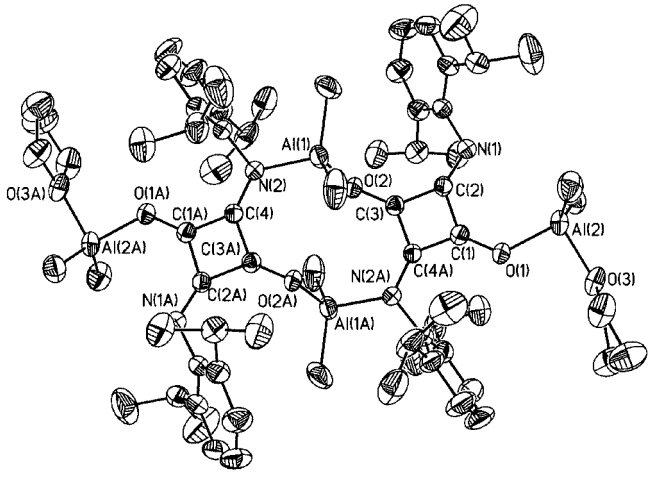

Figure 1. Molecular structure of $L_2(AlMe_2)_4$·2THF·2toluene [L = bis(2,6-diisopropylanilino)squaraine] (**2**) in the crystal (40% probability thermal ellipsoids); toluene molecules and hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles (deg.): C(1)−C(2) 1.471(3), C(2)−C(3) 1.483(3), C(1)−C(4A) 1.428(3), C(3)−C(4A) 1.446(3), C(1)−O(1) 1.279(2), C(3)−O(2) 1.267(3), C(2)−N(1) 1.281(3), N(2)−C(4) 1.335(3), Al(1)−O(2) 1.835(2), Al(2)−O(1) 1.823(2), Al(1)−N(2) 1.916(2); O(2)−Al(1)−N(2) 102.80(8), C(1)−O(1)−Al(2) 127.97(13), C(3)−O(2)−Al(1) 131.16(14), C(2)−N(1)−C(11) 119.82(18), C(4)−N(2)−Al(1) 125.16(14), C(1)−C(2)−C(3) 85.80(15), C(4A)−C(3)−C(2) 91.80(17)

covalent in nature, with a typical bond length of 1.916(2) Å. The average bond angle around N is 119.5°. The lone pairs on the O atoms coordinate to the Al atom by forming an Al−O coordinative bond. This may account for the formation of a dimer of the complex instead of a monomer, since the bond character of the O and N of the same squaraine ligand is different, and Al is more oxophilic. The two Al atoms within the ring adopt a typical tetrahedral geometry with an average bond angle of 109.3° at Al.

There are some noticeable differences in the structure of the squaraine ligands in complex **2** compared to those reported previously.[2b,2c,6] The C(2)−N(1) bond length of 1.281(3) Å is typical of a C=N double bond (1.273 Å in CH_2=NH[8]). Apparently, N(1) is sp^2 hybridized with a C(2)−N(1)−C(11) bond angle of 119.82(2)°. The C(4)−N(2) bond length of 1.335(3) Å is longer than a double bond but much shorter than a single bond (1.472 Å[9]). The C(1)−O(1) bond length of 1.279(2) Å is also much shorter than a single bond (1.426 Å[9]). These bonding characteristics can be explained by the p-π conjugation of the lone pairs on O(1) and N(2) and the carbon p orbital.[10] Like previously reported squaraines, the C atoms in the four-membered ring in **2** are all sp^2 hybridized.[2b] Delocalization of the electrons is believed to exist, and this accounts for the longer C(1)−C(4A) double bond [1.428(3) Å]. The C(1)−C(2) [1.471(3) Å], C(3)−C(4A) [1.446(3) Å], and C(2)−C(3) bond lengths [1.483(3) Å] are in the range of a C−C single bond (1.466 Å).[2b] This C-C bonding character of **2** is different from that of the reported bis(dimethylamino)squaraine[6] and dipiperidinosquaraine[2b] in which the C-C bond lengths are almost equal. This may stem from the formation of the organometallic complex of the squaraine.

In summary, bis(2,6-diisopropylanilino)squaraine shows many novel characters when it is adopted as a ligand for an aluminum complex. The rich chemistry of this ligand and its corresponding organometallic complexes have prompted us to carry out further investigation.

Experimental Section

Preparation of Complex 1: 2,6-Diisopropylaniline (9.8 mL, 52 mmol) was added to a suspension of squaric acid (2.80 g, 25 mmol) in ethanol (80 mL) at room temperature. After several minutes a few drops of formic acid were added to the suspension to form a clear colorless solution. The resulting solution was refluxed for 2 days to give a pale-yellow solution. The volatiles were then removed in vacuo to give **1** as a pale-yellow powder. Yield: 4.24 g (40%). Mp: 380 °C (decomp.). EI-MS: *m/z* (%) = 432 (38) [M^+], 417 (48) [$M^+ - CH_3$], 389 (100) [$M^+ - C_3H_7$]. ^{1}H NMR (200 MHz, [D_8]THF): δ = 1.16 (d, 12 H, CHMe_2), 1.25 (d, 12 H, CHMe_2), 3.19 (sept, 4 H, C*H*Me_2), 7.11 (m, 6 H, Ar*H*), 10.30 (s, 1 H, N*H*) ppm; N^+H was not observed. ^{13}C NMR (125.77 MHz, [D_8]THF): δ = 25.06, 25.54 (CHMe_2), 30.33 (*C*HMe_2), 67.22,

67.56, 67.73, 67.91 (squaraine carbon), 123.71, 128.68, 133.80, 146.25 (*Ar*) ppm. IR (Nujol mull): $\tilde{\nu}$ = 1598 cm^{-1} (squaraine carbonyl), 2870 (N^+H), 3151 (N−H). $C_{28}H_{36}N_2O_2$ (432): calcd. C 77.67, H 8.32, N 6.47; found C 77.61, H 8.38, N 6.55.

The experiments below were performed using standard Schlenk techniques or in a glove box under a purified nitrogen atmosphere. Solvents were dried according to standard methods and freshly distilled prior to use.

Preparation of Complex 2: $AlMe_3$ (1.5 mL, 2 M solution in heptane, approx. 2 equiv.) was added to a suspension of **1** (0.70 g, 1.6 mmol) in THF (20 mL) at −78 °C. The suspension was warmed slowly to room temperature and stirred overnight to give a clear yellow solution. All the volatiles were removed in vacuo and the residue was recrystallized from THF/toluene (1:1) at 0 °C to give pale-yellow crystals of **2**. Yield: (0.68 g, 60%). Mp: 190 °C (decomp.). EI-MS: *m/z* (%) only small fragments. ^1H NMR (200 MHz, $CDCl_3$): δ = −1.51 (s, 12 H, Al-*Me*), −0.79 (s, 12 H, Al-*Me*), 1.07−1.17 (m, 48 H, CH*Me*$_2$), 1.85 (s, 8 H, *THF*), 2.94 (sept, 4 H, C*H*Me_2), 3.03 (sept, 4 H, C*H*Me_2), 3.75 (s, 8 H, *THF*) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = −10.24, −9.06 (Al-*Me*), 23.62, 24.02, 24.40, 24.50, 24.61, 24.81, 25.01, 25.10, 25.72, 25.75, 26.45 (CH*Me*$_2$), 29.30, 29.37 (*C*HMe_2), 25.16, 69.71 (*THF*), 77.72, 77.98, 78.18, 78.23 (*squaraine carbon*), 124.36, 124.65, 124.76, 124.94, 127.39, 128.07, 138.32, 140.50, 143.29, 144.95, 169.19 (*Ar*) ppm. IR (Nujol mull): $\tilde{\nu}$ = 1594 cm^{-1} (squaraine carbonyl). $C_{86}H_{124}Al_4N_4O_6$ (1417.81): calcd. C 72.85, H 8.82, N 3.95; found C 71.31, H 8.62, N 3.95.

X-ray Crystallographic Study of 2·2toluene: Crystal dimensions 0.30 × 0.20 × 0.15 mm^3, $C_{86}H_{124}Al_4N_4O_6$, M_r = 1417.81, triclinic, space group $P\bar{1}$, a = 10.3468(12) Å, b = 15.0508(17) Å, c = 15.6447(16) Å, α = 114.243(8)°, β = 99.359(9)°, γ = 96.321(9)°, V = 2149.1(4) $Å^3$, Z = 1, $\rho_{calcd.}$ = 1.095 $Mg·m^{-3}$, F(000) = 768, 1.58 < θ < 24.77°; of 22118 reflections collected, 7304(R_{int} = 0.0812) were independent. The R values are $R1$ = 0.0501 and $wR2$ = 0.1164 [$I > 2\sigma(I)$]; max./min. residual electron density: 0.509/−0.276 $e·Å^{-3}$.

CCDC-193657 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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