



Alumazene adducts with acetonitrile: Structure and thermal stability



Dmitry A. Doinikov^{a,1}, Iva Kollhammerova^{b,1}, Jiri Löbl^b, Marek Necas^{b,c},
Alexey Y. Timoshkin^{a,**}, Jiri Pinkas^{b,c,*}

^a Inorganic Chemistry Group, Institute of Chemistry, St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034, Russia

^b Department of Chemistry, Faculty of Science, Masaryk University, Kotlarska 2, CZ-61137, Brno, Czech Republic

^c Central European Institute of Technology (CEITEC), Masaryk University, Kamenice 5, CZ-62500, Brno, Czech Republic

ARTICLE INFO

Article history:

Received 29 July 2015

Received in revised form

20 February 2016

Accepted 26 February 2016

Available online 27 February 2016

Keywords:

Alumazene

Acetonitrile

Polyfunctional Lewis acids

Tensimetric method

Computational quantum chemistry

DFT

ABSTRACT

Lewis acid-base adducts of the “inorganic analog of benzene” alumazene $[(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3\text{NAlMe})_3]$ (**1**) with acetonitrile (CH_3CN , acn) and deuterioacetonitrile (CD_3CN , $\text{d}_3\text{-acn}$) were synthesized, spectroscopically characterized, and their molecular structures were elucidated by the X-ray diffraction analysis as a bis-adduct **1**(acn)₂ and a tris-adduct **1**($\text{d}_3\text{-acn}$)₃. The thermodynamics of complex formation was investigated experimentally and theoretically. Thermodynamic characteristics of process **1**(acn)₂·acn (s) = **1**(acn)₂ (s) + 2 acn (g) in the temperature range 294–370 K have been derived from the vapor pressure–temperature dependence measurements by the static tensimetric method. It is shown that above 435 K in the presence of **1** gaseous acn undergoes irreversible polymerization reaction. Quantum chemical computations at B3LYP/6-311G(d,p) level of theory have been performed for the **1**(acn)_n and model complexes of $[(\text{HAlNH})_3]$ (**1m**), **1m**(acn)_n ($n = 1\text{--}3$). Obtained results indicate that for the gas phase adducts upon increasing the number of acn ligands the donor-acceptor Al–N(acn) distances increase in accord with decrease of the donor-acceptor bond dissociation energies.

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1. Introduction

A theoretical study showed that borazine $[(\text{HBNH})_3]$ should prefer formation of donor-acceptor complexes with Lewis acids while its adducts with Lewis bases are unstable [1]. This is substantiated in triorganylborazines $[(\text{RBNH})_3]$ (R = Me, Et, *i*-Pr, *t*-Bu, Ph) that form 1:1 adducts with AlBr_3 and GaCl_3 [2]. In contrast, alumazenes $[(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3\text{NAlR})_3]$ (**1**, Me, **2**, SiMe₃) [3–5] feature reactivity much different from borazine [6–11]. The previously studied reactions between **1** and Lewis bases provided crystalline mono- and bis-adducts in the case of OPPh_3 [12] and $\text{OP}(\text{OMe})_3$ [13], and bis- and tris-adducts in reactions with pyridine and dimethylaminopyridine (DMAP) [14]. Substituted benzonitriles provide only bis-adducts in *cis* or *trans* configuration. These 1:2 adducts are formed even in the presence of excess base [15,16]. One reason could be the decreasing Lewis acidity of the third Al atom

upon coordination of two molecules of nitrile to the alumazene ring. There could be also the steric hindrance by the bulky 2,6-(*i*-Pr)₂C₆H₃ (Dipp) groups at nitrogen atoms of **1**. However, the reaction between **1** and isobutyronitrile produces a tris-adduct [15]. The adducts of **1** with Lewis bases can be used as starting compounds for the preparation of cations of alumazene as these species would be additionally stabilized in comparison to the cations of uncoordinated **1**. Therefore we decided to study a simple nitrile, CH_3CN (acn), in reactions with **1** in different molar ratios. Synthetic effort was directed towards establishing the molecular structure of isolated products. Furthermore we studied thermodynamic characteristics of adduct dissociation process by the tensimetry method and used quantum chemical computations to establish stability of adducts of **1** with acetonitrile and its sterically unhindered model compound $[(\text{HAlNH})_3]$ (**1m**).

2. Experimental section

2.1. General procedures

All manipulations were performed under a dry nitrogen atmosphere by Schlenk techniques or in a MBraun Unilab dry box maintained under 1 ppm of O₂ and H₂O. Solvents were dried over

* Corresponding author. Department of Chemistry, Faculty of Science, Masaryk University, Kotlarska 2, CZ-61137, Brno, Czech Republic.

** Corresponding author.

E-mail addresses: a.y.timoshkin@spbu.ru (A.Y. Timoshkin), jpinkas@chemi.muni.cz (J. Pinkas).

¹ These authors contributed to the work equally.

and distilled from Na/benzophenone under nitrogen. Toluene-*d*₈ was dried over and distilled from Na/K alloy while P₄O₁₀ was used for CDCl₃, and CD₂Cl₂. CD₃CN and CH₃CN were dried over molecular sieves. Solvents were degassed prior to use. Alumazene was prepared by a modified procedure from AlMe₃ and 2,6-diisopropylaniline [17]. NMR spectra (¹H, ¹³C, ²⁷Al) were acquired on Avance DRX 500 and 300 MHz spectrometers. Chemical shifts were referenced to the residual protic impurities or solvent resonances (¹H and ¹³C) or externally to Al(acac)₃ in C₆D₆ (²⁷Al). The IR spectra (4000–400 cm⁻¹) were collected on Bruker EQUINOX 55/S/NIR and TENSOR 27 FTIR spectrometers. Samples were prepared as KBr pellets. Raman spectra were obtained on a FT-IR spectrometer BRUKER EQUINOX IFS 55/S with a Raman stage FRA 106/S. Excitation was induced by a Nd:YAG laser (1064 nm, max. power 500 mW). Samples were measured directly in Schlenk flasks or in glass capillaries (o.d. 1.5 mm). CHN elemental analyses were carried out by Analytisches Labor der Anorganischen Instituts of Göttingen University. Melting points were measured in sealed capillaries and are uncorrected. Single-crystal diffraction data for **1**(acn)₂ were collected on a KUMA KM-4 κ-axis CCD diffractometer with graphite-monochromated Mo-Kα radiation. Diffraction data for **1**(d₃-acn)₃·2d₃-acn were collected on a Rigaku MicroMax-007 HF rotating anode four-circle CCD diffractometer with Mo-Kα radiation. *CrystalClear* [18] and *CrysAlisPro* [19] software packages were used for data collection and data reduction. The structure was solved using *SHELXS* program and refined (full matrix least-squares refinement on *F*²) using *SHELXL* program [20]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at calculated positions and refined as riding on their carrier atoms.

Details of the data collection and refinement are summarized in Table 1.

2.2. Synthesis of **1**(acn)₂

To the solution of **1** (0.497 g, 0.762 mmol) in dry deoxygenated toluene (15 mL), acetonitrile (acn) (0.12 g, 2.9 mmol) was added. The reaction mixture was stored at –25 °C and after a month, the

colorless crystals were obtained. Filtration and drying under vacuum at room temperature for 3.5 h provided compound **1**(acn)₂ (0.237 g, 42.4%). M.p.: 207–209 °C. ¹H NMR (*d*₈-toluene, 300 MHz): δ 7.18–7.01 (m, 9H, H_{arom}), 4.14 (sept, *J* = 7.0 Hz, 6H, CH(CH₃)₂), 1.35 (d, *J* = 6.8 Hz, 36H, CH(CH₃)₂), 0.81 (s, 6H, CH₃CN), –0.84 (s, 9H, Al–CH₃). ¹H NMR (CDCl₃, 300 MHz): δ 7.03 (d, *J* = 7.8 Hz, 6H, m-H_{arom}), 6.89 (t, *J* = 7.8 Hz, 3H, p-H_{arom}), 3.94 (sept, *J* = 7.0 Hz, 6H, CH(CH₃)₂), 2.25 (s, 6H, CH₃CN), 1.24 (d, *J* = 7.0 Hz, 36H, CH(CH₃)₂), –1.20 (s, 9H, Al–CH₃).

¹³C APT NMR (CD₃CN + toluene, 500 MHz): δ 145.22 (s, 2-C_{arom}), 137.96 (s, 1-C_{arom}), 122.66 (s, 4-C_{arom}), 122.54 (s, 3-C_{arom}), 117.14 (s, CD₃CN), 27.59, 27.03 (s, CH), 25.70, 22.10 (s, CH₃), 0.34 (sept, *J* = 20.8 Hz, CD₃CN), –8.5 (br s, Al–CH₃).

²⁷Al NMR (CD₃CN, 500 MHz): δ 69.4 ppm.

IR (KBr, cm⁻¹): ν 3416 m br, 3047 m, 2961 vs, 2922 s, 2866 m, 2363 w, 2350 vw, 2315 w, 2288 w, 1458 m, 1425 s, 1383 w, 1314 m, 1258 m, 1234 m, 1180 vs, 1103 s, 1040 s, 903 vs, 866 s, 791 vs, 721 m, 662 m, 623 m.

Raman: ν 3043 m, 3004 s, 2933 vs, 2866 s, 2305 vs, 2261 m, 2244 m, 2205 w, 2108 vs, 2103 vs, 1585 s, 1463 s, 1446 s, 1241 s, 1099 w, 1039 s, 888 m, 865 m br, 703 w, 577 w.

Anal. Calcd for C₄₃H₆₆Al₃N₅ (733.97): C, 70.37; H, 9.06; N, 9.54. Found: C, 70.07; H, 9.05; N, 9.35%.

2.3. Synthesis of **1**(d₃-acn)₃

To the solution of **1** (0.155 g, 0.238 mmol) in dry deoxygenated toluene (10 mL), CD₃CN (0.814 g, 18.5 mmol) was added. The reaction mixture was stirred for 3.5 h at room temperature. The reaction mixture was stored at room temperature and, after a week, the colorless crystals were obtained. Crystals for the X-ray diffraction analysis were used directly from the mother liquor.

2.4. Vapor pressure measurements

A series of vapor pressure–temperature dependence measurements have been performed by the static tensimetry method with a glass membrane null-manometer [21,22]. This technique is applicable for studying both heterogeneous and (after complete vaporization of the sample) homogeneous gas phase equilibria. The pressure was measured with accuracy of 0.1 Torr with an MChR-3 mercury manometer. The temperature with ±0.05 °C accuracy was determined by two chromel–alumel thermocouples (thermoEDF was measured by a V36 voltmeter). The volume of the membrane chamber was found from the difference in weights of water-filled and empty systems. The error in volume determination amounts ±0.02 mL. Because of the high air and moisture sensitivity, introduction of the samples in all experiments has been performed in a glass apparatus under vacuum (~10⁻⁵ Torr).

2.5. Quantum chemical computations

All computations were performed using DFT hybrid functional B3LYP [23,24] in conjunction with all electron triple zeta quality 6-311G(d,p) basis set. Similar computational approach was used in our previous work on the alumazene–pyridine system [14]. Structures of all compounds were fully optimized and verified by vibrational analysis to be minima on their respective potential energy surfaces (PES). We encountered convergence problems for the geometry optimization of **1**. In this case, the geometry of the lowest energy structure obtained during optimization with Opt = CalcAll was used for the analysis. Standard enthalpies were obtained taking into account zero point energies and thermal corrections. GAUSSIAN 09 program package [25] was used throughout. Basis set superposition error was computed using counterpoise

Table 1
Crystallographic data and structure refinement parameters for **1**(acn)₂ and **1**(d₃-acn)₃·2d₃-acn.

Compound	1 (acn) ₂	1 (d ₃ -acn) ₃ ·2d ₃ -acn
Empirical formula	C ₄₃ H ₆₆ Al ₃ N ₅	C ₄₉ H ₆₀ D ₁₅ Al ₃ N ₈
fw	733.95	872.20
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> _{21/c}	<i>P</i> ₂₁₂₁₂₁
Temperature, K	120(2)	120(2)
λ, Å	0.71073	0.71075
<i>a</i> , Å	16.101(7)	12.23310(10)
<i>b</i> , Å	11.902(6)	13.4984(2)
<i>c</i> , Å	24.092(13)	31.3617(4)
α, deg	90	90
β, deg	103.79(4)	90
γ, deg	90	90
<i>V</i> , Å ³	4484(4)	5178.67(11)
<i>Z</i>	4	4
μ, mm ⁻¹	0.118	0.112
No. of refls collected	30377	28009
No. of indep. refls (<i>R</i> _{int})	7877 (0.0185)	9843 (0.0249)
No. of data/restraints/parameters	7877/0/477	9843/0/561
GoF on <i>F</i> ²	0.966	1.040
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0415, 0.0900	0.0312, 0.0755
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0935, 0.1110	0.0342, 0.0774
Largest diff. peak/hole, e ⁻ Å ⁻³	0.294/–0.234	0.217/–0.223

^a *R*₁ = Σ||*F*_o|| – ||*F*_c||/Σ||*F*_o||.

^b *wR*₂ = [Σ*w* (*F*_o² – *F*_c²)/Σ(*F*_o²)^{1/2}].

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