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Alumoxane Hydride and Aluminum Chalcogenide Hydride Compounds with Pyrazolato Ligands[**]

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Dedicated to Professor Marianne Baudler
on the occasion of her 80th birthday

Since 1980 intense interest in alkylalumoxanes has been generated primarily from the work of Sinn and Kaminsky,[1] who found methylalumoxane (MAO) to be a good cocatalyst for the transition metal catalyzed polymerization of alkenes.[1–3] Although the role of MAO seems to be understood,[4] the structure of the catalytically active species of methylalumoxane remains unknown. Especially the coordination number of the aluminum center is still a question of debate. Recently, several alumoxanes $(t\mathrm{BuAlO})_n$ ($n = 6-9$) and aluminum hydroxides (aluminum oxide hydroxides) displaying a lower degree of aggregation were prepared by the reaction of R_3Al (R = *t*Bu, Me, 2,4,6-$Me_3C_6H_2$ (Mes), Ph) with water or anhydrous lithium hydroxide.[5, 6] On the other hand, it has been shown that aluminum hydride compounds can be used as precursors for the synthesis of organoaluminum chalcogenides with the formula $(\mathrm{RAlE})_n$ (R = organic group; E = O, S, Se, Te) upon reaction with species such as $(Me_2SiO)_3$,[7] $S(SiMe_3)_2$,[8] Se(Te),[9a, 10] or $(RE)_2$ (E = Se, Te).[9b] The recent results in the chemistry of 3,5-*tert*-butylpyrazolatoaluminum dihydride ($[\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz}(\mu\text{-Al})\mathrm{H_2}]_2$ (**1**))[11] prompted us to synthesize compounds of the formula $[(\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz}(\mu\text{-Al})\mathrm{H})_2\mathrm{E}]_n$ (E = O (**2**) ($n = 2$); S (**3**), Se (**4**), Te (**5**) ($n = 1$)). Herein we present the molecular structures of **2**–**5**. To the best of our knowledge, **2** represents the first example of a structurally characterized alumoxane hydride in which two of the Al atoms are five-coordinate. Product **3** is the first compound prepared by the reaction involving aluminum hydride and elemental sulfur.

A solution of compound **1** in dry dioxane was stirred at room temperature for five days to yield **2** (Scheme 1). The X-ray crystal structure of **2** confirms the tetrameric arrangement (Figure 1),[12] as also indicated for the gas phase by the MS(EI) spectrum (*m*/*z* 860). The Al_2O_2 core of the molecule consists of a quite regular parallelogram, and interestingly all the Al and O atoms are coplanar (the sum of angles at O is 359.98(22)°). Each oxygen atom is connected to three AlH groups to form a μ_3-O bridge. The Al atoms located outside

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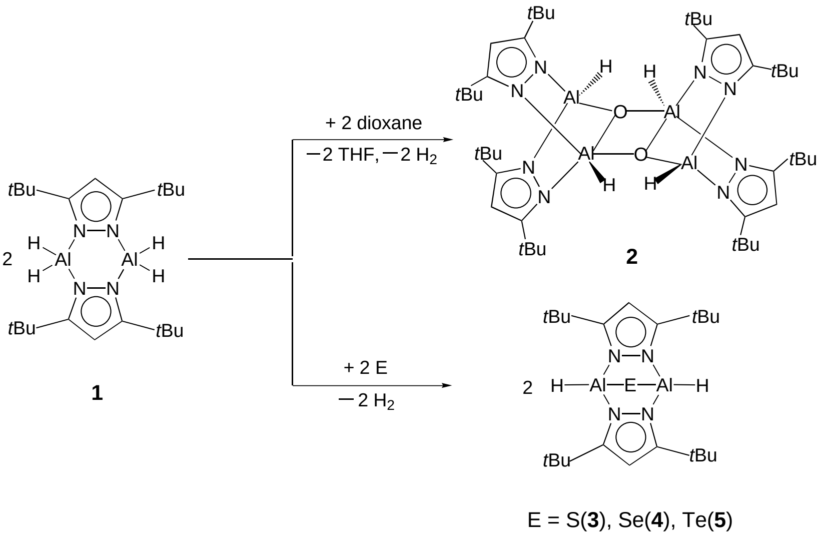

Scheme 1. Syntheses of compounds **2**–**5**.

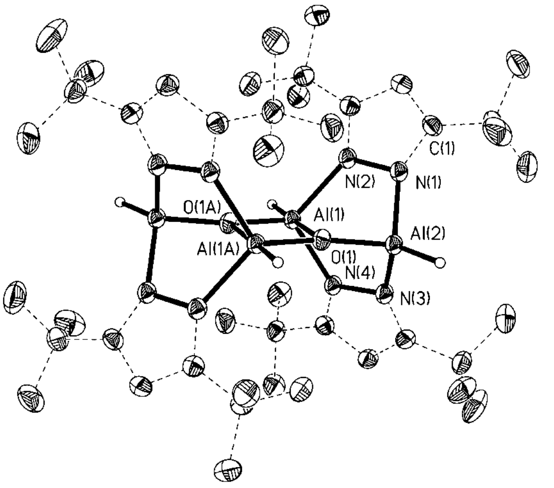

Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Al(1)–O(1) 1.922(2), Al(1)–O(1A) 1.786(2) Al(2)–O(1) 1.7260(14); Al(1A)-O(1)-Al(2) 155.08(8), Al(1)-O(1)-Al(2) 105.07(7), Al(1)-O(1)-Al(1A) 99.83(7), O(1)-Al(1)-O(1A), 80.17(7).

the parallelogram use two μ-η^1-η^1 pyrazolato ligands to form two six-membered Al_2N_4 rings in a boat conformation. As already mentioned, the interesting feature of **2** is the coordination number five at the Al atoms in the Al_2O_2 core; this differs from other characterized alumoxanes in which the Al atoms usually show coordination numbers of three and four.[5a,b, 6, 7] Only one structurally characterized alumoxane hydroxide containing five-coordinate Al atoms has been published.[5c] Reports of compounds[13] with coordination numbers five,[13a,b] six,[13c] and even seven[13d] at Al have appeared in the literature, but these systems involve multi-chelating ligands such as a tetradentate Schiff base, $N(CH_2CH_2OH)_3$, and crown ether. In compound **2** significantly longer bond lengths and smaller angles are observed at the five-coordinate Al(1) compared to the four-coordinate Al(2) (Figure 1). The bond lengths of Al(1)–O(1A) (1.786(2) Å) and Al(2)–O(1) (1.7260(14) Å) are shorter than the sum of the covalent radii.[14] The Al(1A)-O(1)-Al(2) angle of 155.08(8)° is significantly larger than the Al-O-Al angle in $[Al_6tBu_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4]$ (103.7(9)°)[5c] and in $(Mes^*AlO)_4 \cdot 2\,C_6H_6$ (151.32(13)°; Mes* = 2,4,6-$tBu_3C_6H_2$).[7]

The ^1H NMR spectrum of **2** shows only one set of signals ($\delta = 1.32$, 5.80), implying the existence of dynamic processes in solution. The GC-MS(EI) investigations on the reaction solution of **2** indicate the formation of THF. Accordingly, we assume that the formation of **2** proceeds by nucleophilic attack at the aluminum center of **1** by one of the oxygen atoms of dioxane and then insertion into an Al–H bond, leading to the degradation of dioxane and formation of an Al–O bond in **2**. However, the use of other oxygen-transfer reagents such as nBu_2SnO leads to small amounts of **2** including several by-products.

Treatment of **1** in toluene with the congeners of oxygen affords three chalcogenide compounds of type $[\{\eta^1\text{-}3,5\text{-}tBu_2pz(\mu\text{-}Al)H\}_2E]$ (E = S (**3**), Se (**4**), Te (**5**); Scheme 1). It is important, especially for the preparation of **3**, to use strictly equivalent amounts of the reactants and the mixed solvent system (THF/toluene 1/9), otherwise an insoluble polymeric material is formed. This might explain why the reaction of aluminum hydride with sulfur has not yet been reported. All compounds, especially **4** and **5**, are very susceptible to oxygen. Small amounts of air immediately lead to the decomposition of **4** and **5**. An attempt to substitute all the H atoms at the Al atoms of **1** with two equivalents of Se results in the homoleptic compound $[Al(\eta^2\text{-}3,5\text{-}tBu_2pz)_3]$.[15]

X-ray crystallography reveals the compounds **3**–**5** to be isostructural. They are represented by the illustration of **3** in Figure 2.[12] Compound **3** consists of a boat-shaped, six-membered Al_2N_4 ring. A sulfur atom forms a bridge between the two Al atoms and one Al–H bond remains at each Al center. Two pyrazolato ligands are located on the same side of the molecule due to the constraint of the sulfur atom. The

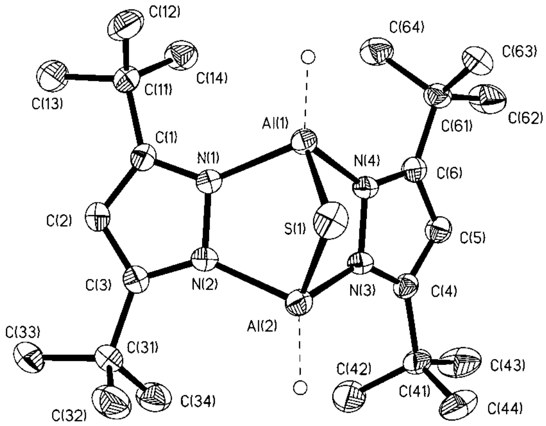

Figure 2. Molecular structure of **3**. The structures of **4** and **5** are analogous with Se(1) (**4**) and Te(1) (**5**) in place of S(1). Selected bond lengths [Å] and angles [°]. **3**: S(1)–Al(1) 2.2080(6), S(1)–Al(2) 2.2117(7), Al(1)–N(1) 1.9469(12); Al(1)-S(1)-Al(2) 79.58(2). **4**: Se(1)–Al(1) 2.3449(10), Se(1)–Al(2) 2.3574(11), Al(1)–N(1) 1.932(2); Al(1)-Se(1)-Al(2) 75.78(3). **5**: Te(1)–Al(1) 2.5763(11), Te(1)–Al(2) 2.5621(12), Al(1)–N(1) 1.944(3); Al(1)-Te(1)-Al(2) 69.41(3).

average Al–E bond length (**3**: Al–S 2.1099(7); **4**: Al–Se 2.3511(10); **5**: Al–Te 2.5692(11) Å) is not only slightly shorter than those in $(Mes^*AlS)_2$ (2.2095(11) Å),[8b] $[Me_3NAl(SeEt)_3]$ (2.357(8) Å),[9a] and $[Me_3NAl(TePh)_3]$ (2.585(2) Å),[9a] but also shorter than the sum of the covalent radii. The Al-E-Al angles in **3** (79.58(2)° and **4** (75.78(3)°) are close to those in $(Mes^*AlS)_2$ (78.09(3)°)[8b] and $[\{N(SiMe_3)C(Ph)C(SiMe_3)_2Al(\mu\text{-}Se)\}_2]$ (77.58(3)°),[10a] whereas the Al-Te-Al angle in **5** (69.41(3)°) is significantly smaller than that in $[\{N(SiMe_3)C(Ph)C(SiMe_3)_2Al(\mu\text{-}Te)\}_2]$ (76.88(4)°).[10a] The Al-E-Al unit (E = O (Al(1)-O(1)-Al(2)), S, Se, Te) shows a more acute angle upon going from the lighter to the heavier congeners.

The reaction leading to the formation of **3**–**5** probably proceeds via an Al-E-H intermediate. This species then reacts with one of the H atoms at another Al center, and subsequently forms the Al-E-Al bridge and H_2 (Scheme 1). This assumption is supported by the recent results on fully characterized Al–SeH compounds.[10b]

The higher aggregation of **2** compared to **3**–**5** is probably due to the increased nucleophilicity of oxygen versus the heavier congeners. Therefore compound **2** might function as a molecular alternative to MAO. This work is presently in progress.

Experimental Section

2: A solution of **1** (0.83 g, 2.0 mmol) in dry dioxane (50 mL) was stirred for five days at room temperature and then filtered through celite. The filtrate was reduced to about 10 mL, and compound **2** was isolated as colorless crystals at room temperature (3–4 weeks, 15–25%). Single crystals suitable for X-ray diffraction analysis were obtained from dioxane at room temperature. M.p. 240–243 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.32$ (s, 72H; *t*Bu), 4.8 (very br, 4H; AlH, $w_{1/2} = 80$ Hz), 5.80 (s, 4H; CH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 31.19$ (s; Me), 32.29 (s; CMe_3), 101.09 (s; CH), 163.31 (s; *Ct*Bu); MS (EI): *m/z* (%): 860 ([M^+], 100).

3: Toluene and THF (50 mL, 9/1) were added to equivalent amounts of **1** (0.83 g, 2.0 mmol) and sulfur (0.064 g, 2.0 mmol; dried before use), and the suspension was stirred at 50 °C for 15 h and then filtered through celite. The filtrate was concentrated to about 10 mL, and THF (2 mL) was added to precipitate **3** as colorless crystals at room temperature (0.52 g, 58%). M.p. > 230 °C (decomp); ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.33$ (s, 36H; *t*Bu), 5.97 (s, 2H; CH), 5.6 (very br, 2H; AlH); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 31.17$ (s; Me), 32.40 (s; CMe_3), 102.25 (s; CH), 165.30 (s; *Ct*Bu); MS (EI): *m/z* (%): 446 ([M^+], 98), 445 ([$M^+ - H$], 100); elemental analysis (C, H, N) correct for $C_{22}H_{40}Al_2N_4S$.

4: Toluene (50 mL) was added to equivalent amounts of **1** (0.83 g, 2.0 mmol) and Se (0.16 g, 2.0 mmol; used as black powder as received), and the suspension was refluxed for 2–3 h until the black selenium disappeared. The resulting solution was filtered through celite and concentrated to about 10 mL to afford colorless crystals at 4 °C (0.61 g, 62%). M.p. 272 °C; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.33$ (s, 36H; *t*Bu), 5.98 (s, 2H; CH), 5.7 (very br, 2H; AlH); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 31.08$ (s; Me), 32.45 (s; CMe_3), 102.57 (s; CH), 165.25 (s; *Ct*Bu); MS (EI): *m/z* (%): 494 ([M^+], 80), 491 ([$M^+ - 3H$], 100); elemental analysis (C, H, N) correct for $C_{22}H_{40}Al_2N_4Se$.

5: Toluene (50 mL) was added to equivalent amounts of **1** (0.83 g, 2.0 mmol) and Te (0.26 g, 2.0 mmol; used as black powder as received), and the suspension was refluxed for four days until most of the Te disappeared. The solution was filtered through celite and concentrated to about 10 mL to give colorless crystals at 4 °C (0.58 g, 54%). M.p. 250–251 °C; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.35$ (s, 36H; *t*Bu), 5.98 (s, 2H; CH), 5.7 (very br, 2H; AlH); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 30.94$ (s; Me), 32.58 (s; CMe_3), 103.24 (s; CH), 165.05 (s; *Ct*Bu). MS (EI): *m/z* (%): 542 ([M^+], 100); elemental analysis (C, H, N) correct for $C_{22}H_{40}Al_2N_4Te \cdot 0.85$ toluene.

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[12] X-ray crystal structure determination: The data for **2**–**5** were collected on a Stoe-Siemens four-circle diffractometer (at −70(2) °C) with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined against F^2 on all data by full-matrix least squares with SHELXS-97.[16] **2** ($C_{56}H_{104}Al_4N_8O_8$; includes three dioxane molecules): $M_r = 1125.39$, triclinic, space group $P\bar{1}$, $a = 10.202(5)$, $b = 13.128(6)$, $c = 13.612(5)$ Å, $\alpha = 112.39(3)$, $\beta = 101.90(2)$, $\gamma = 96.936(13)°$, $V = 1608.7(12)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.162$ Mg m^{-3}, $F(000) = 612$, $\mu(Mo_{K\alpha}) = 0.127$ mm^{-1}. A total of 9401 reflections were measured in the range $7.20 \leq 2\theta \leq 50.08°$, of which 5673 were unique. Final *R* indices: $R_1 = 0.0404$ ($I > 2\sigma(I)$), $wR_2 = 0.1113$ (all data); max./min. residual electron density 307/−253 e nm^{-3}. **3** ($C_{22}H_{40}Al_2N_4S$): $M_r = 446.6$, monoclinic, space group $P2_1/n$, $a = 14.407(2)$, $b = 11.0570(14)$, $c = 16.506(3)$ Å, $\beta = 98.54(2)°$, $V = 2600.1(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.141$ Mg m^{-3}, $F(000) = 968$, $\mu(Mo_{K\alpha}) = 0.207$ mm^{-1}. A total of 9761 reflections were measured in the range $7.02 \leq 2\theta \leq 50.06°$, of which 4581 were unique. Final *R* indices: $R_1 = 0.0301$ ($I > 2\sigma(I)$), $wR_2 = 0.0870$ (all data); max./min. residual electron density 263/−183 e nm^{-3}. **4** ($C_{22}H_{40}Al_2N_4Se$): $M_r = 494$, monoclinic, space group $P2_1/n$, $a = 14.385(3)$, $b = 11.035(2)$, $c = 16.522(3)$ Å, $\beta = 98.90(3)°$, $V = 2591.1(9)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.265$ Mg m^{-3}, $F(000) = 1040$, $\mu(Mo_{K\alpha}) = 1.532$ mm^{-1}. A total of 5301 reflections were measured in the range $4.46 \leq 2\theta \leq 52.74°$, of which 5301 were unique. Final *R* indices: $R_1 = 0.0415$ ($I > 2\sigma(I)$), $wR_2 = 0.1474$ (all data); max./min. residual electron density 551/−944 e nm^{-3}. **5** ($C_{29}H_{48}Al_2N_4Te$; includes one toluene molecule): $M_r = 634.27$, monoclinic, space group $P2_1/n$, $a = 12.288(2)$, $b = 15.592(3)$,

$c = 18.031(3)$ Å, $\beta = 106.295(14)^\circ$, $V = 3316.1(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.270\ \mathrm{Mg\,m^{-3}}$, $F(000) = 1312$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.972\ \mathrm{mm^{-1}}$. A total of 7932 reflections were measured in the range $7.02 \leq 2\theta \leq 50.04^\circ$, of which 5847 were unique. Final R indices: $R_1 = 0.0389$ ($I > 2\sigma(I)$), $wR_2 = 0.0991$ (all data); max./min. residual electron density 1006/ $-694\ \mathrm{e\,nm^{-3}}$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-145888 (**2**), CCDC-145889 (**3**), CCDC-145981 (**4**), and CCDC-145982 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Stereochemical Assignment of the C21–C38 Portion of the Desertomycin/Oasomycin Class of Natural Products by Using Universal NMR Databases: Prediction[**]

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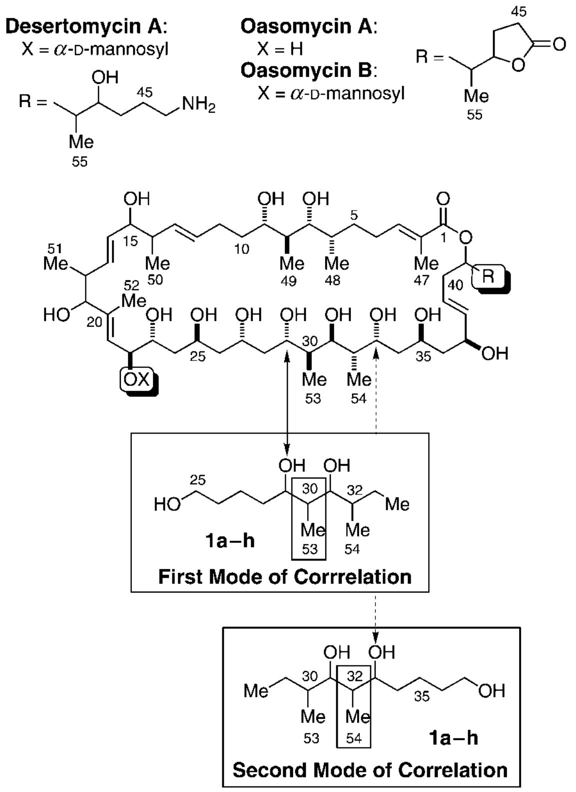
We recently reported our first step toward the creation of a universal NMR database through analysis of a typical structural motif often found in polypropionate natural products.[1] We then demonstrated the reliability and usefulness of such an NMR database by using the C5–C10 portion of the desertomycin/oasomycin class of natural products.[2] In this and the following paper,[3] we report a further development of this approach by predicting, and proving, the stereochemistry of the C21–C38 portion of the desertomycin/oasomycin class of natural products.[4]

The C29–C33 portion of desertomycins/oasomycins is viewed as a contiguous dipropionate unit so that our propionate database[1] could be applied to predict its stereochemistry. There are apparently two modes of correlation of the NMR database with this portion of desertomycins/oasomycins (see the lower half of Scheme 1). By following the same procedure described previously,[2] we have compared the ^{13}C NMR characteristics of the C29–C32 (first mode of correlation) and C30–C33 (second mode of correlation) portions of the natural products with those of each of the eight diastereomers.[5] As seen from the graphs (Figures 1 and 2), none of the eight diastereomers match the corresponding structural portion of the natural products at a satisfactory level.[6] However, this outcome is not totally surprising when one takes into account the fact that the natural products have additional hydroxyl groups at C27 and C35. As these hydroxyl groups are attached on the contiguous dipropionate unit and linked through a bridge consisting of one methylene group,[7] a significant steric and/or stereoelectronic effect would be expected from them on the basis of NMR characteristics of the structural portion in question. Hence, we chose to focus only on the ^{13}C NMR characteristics of the C30 and C53 (see the smaller box in the first mode of correlation in Scheme 1) and of the C32 and C54 (see the smaller box in the second mode of correlation) portions of the natural products. From these comparisons (Figure 3) one (**1h** = $\alpha\beta\beta\alpha$) and three (**1a** = $\beta\beta\alpha\alpha$, **1f** = $\alpha\alpha\alpha\beta$, and **1h** = $\beta\alpha\alpha\beta$) candidates emerge from the first and second modes of correlation, respectively.



Scheme 1. Structures of desertomycin A and oasomycins A and B, as well as two modes of structural correlation with the contiguous dipropionate NMR database **1a–h**.

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