93-55-0; p-$CF_3C_6H_4CHO$, 455-19-6; p-$CH_3C_6H_4CHO$, 104-87-0; $CH_3O_2CCH_2CH_3$, 554-12-1; CH_3CH_2CHO, 123-38-6; $CH_3CH_2C(O)CH_2CH_3$, 96-22-0; p-$CF_3C_6H_4C(O)CH_2CH_3$, 711-33-1; p-$CH_3C_6H_4C(O)CH_2CH_3$, 5337-93-9; methyl formate, 107-31-3; formaldehyde, 50-00-0; 4-pentenal, 2100-17-6; 3-pentenal, 5604-55-7.

Synthesis and Molecular Structure of the Aluminum–Nitrogen Macrocyclic Cage $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$: Reaction of Disproportionation Products of the Diethylaluminum Chloride Dimer

Gregory H. Robinson* and Samuel A. Sangokoya

Department of Chemistry, Clemson University
Clemson, South Carolina 29634-1905

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Summary: Reaction of diethylaluminum chloride with the macrocyclic tetradentate secondary amine 1,4,8,11-tetraazacyclotetradecane in chlorobenzene affords the crystalline complex $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$. The title compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters a = 11.871 (9) Å, b = 9.052 (7) Å, c = 14.299 (1) Å, β = 115.19 (4)°, and D_{calcd} = 1.31 g cm^{-3} for $Z = 2$. Least-squares refinement based on 1310 observed reflections with intensities $I \geq 3\sigma(I)$ in the range of 2.00° $\leq 2\theta \leq$ 50.0° converged at R = 0.0789 (R_w = 0.0949). The mean Al–N distance in the title compound is 1.956 (6) Å while the mean Al–Cl distance is 2.168 (3) Å.

Although the nitrogen-based macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane[1] was reported decades prior to Pedersen's discovery of dibenzo-18-crown-6[2,3] the chemistry of aza macrocycles has not developed in parallel with that of their oxygen analogues. Nonetheless, the interaction of nitrogen-based macrocyclic ligands with transition-metal ions resulting in unusual or unique coordination complexes has been well-documented in the literature.[4–13]

The interaction of aluminum alkyls with macrocyclic ligands has proven to be a particularly fruitful area of organoaluminum chemistry. The reaction of crown ethers with aluminum alkyls has resulted in several $[AlR_3]_n$·CE (CE = crown ether) complexes.[14–16] The significance of these unusual organometallic products is due to the fact that they often serve as precursors to a class of nonstoichiometric organoaluminum inclusion compounds known as liquid clathrates.[17] An examination of the organoaluminum chemistry of nitrogen- and sulfur-based macrocycles represents an interesting extension of this work. We have reported a series of novel aluminum alkyl–nitrogen[18–21] and –sulfur[22,23] macrocyclic complexes. Herein, we report the synthesis[24] and structure of $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$ isolated from reaction of diethylaluminum chloride with 1,4,8,11-tetraazacyclotetradecane, $C_{10}H_{24}N_4$, in chlorobenzene. In addition to representing the first X-ray structural report of an alkylaluminum halide–macrocyclic amine complex, the title compound is interesting in that it may possibly result from reaction of disproportionation products of diethylaluminum chloride with the macrocycle.

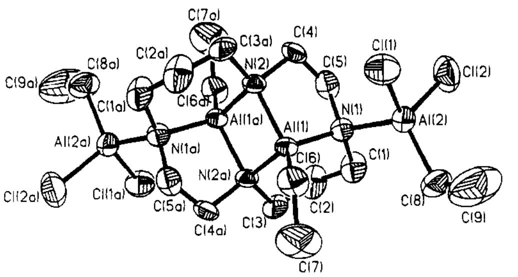

Figure 1. A view of the $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$ molecule showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been omitted.

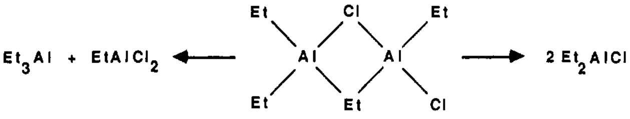

Figure 2. Organoaluminum products resulting from bridge cleavage of the proposed transient mixed alkyl–halo isomer of diethylaluminum chloride.

X-ray intensity data were collected on a Nicolet R3m/V diffractometer using an ω-scan technique with Mo Kα radiation (λ = 0.71073 Å) at 26 °C. The title compound crystallizes in the monoclinic space group $P2_1/n$ with unit

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[24] Reaction of 1,4,8,11-tetraazacyclotetradecane (2.00 mmol) with diethylaluminum chloride (Aldrich Chemical Co.; purity > 97%) (8.00 mmol) in chlorobenzene (25 mL), under an atmosphere of nitrogen, affords the title compound after considerable heating (120 °C) and subsequent cooling. The system was frequently vented to relieve pressure. Upon cooling to room temperature, a multitude of colorless, rectangular, extremely air-sensitive, X-ray quality crystals deposited on the walls of the reaction vessel (in quantitative yield): mp 245 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.164 (q, 4 H, $Al(CH_2CH_3)$), 0.740 (q, 4 H, $Al(CH_2CH_3)$), 1.192 (t, 6 H, $Al(CH_2CH_3)$), 1.444 (t, 6 H, $Al(CH_2CH_3)$). The resonance for the macrocycle consisted of a complex multiplet, δ 2.720–4.340 (m, 20 H).

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cell parameters $a = 11.871$ (9) Å, $b = 9.052$ (7) Å, $c = 14.299$ (1) Å, $\beta = 115.19$ (4)°, and $D_{calcd} = 1.31$ g cm^{-3} for $Z = 2$. Least-squares refinement based on 1310 observed reflections with intensities $I \geq 3\sigma(I)$ in the range of $2.00° \leq 2\theta \leq 50.0°$ converged at $R = 0.0789$ ($R_w = 0.0949$). Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions with fixed isotropic temperature factors.

The title compound bears a striking resemblance to Al_2N_2 condensation products obtained from high-temperature R_2N–H/AlR_3 reactions. Fundamental studies of such reactions of aluminum alkyls with simple monodentate amines were reported by Smith.[25–33] These reactions, referred to as intermolecular condensations, initially produce simple R_2N–H:AlR_3 adducts at room temperature. Increase in reaction temperature, however, results in cleavage of N–H and Al–R bonds, the evolution of alkane, and the subsequent formation of Al_2N_2 fragments in the reaction products.

As can be seen from the X-ray crystal structure of $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$ (Figure 1), the title compound resides on a crystallographic center of symmetry with a planar Al_2N_2 four-membered ring occupying the central cavity of the macrocycle. The Al_2N_2 ring is asymmetric with independent Al–N distances of 1.954 (6) and 1.945 (6) Å for Al(1)–N(2) and Al(1)–N(2a), respectively. The Al(1)···Al(1a) separation of 2.768 (3) Å does not indicate significant metal–metal interaction. Characteristic of compounds containing Al_2N_2 four-membered rings,[29,31,32] the N–Al–N and Al–N–Al bond angles approach 90° (89.6 (3)° and 90.4 (4)° for N(2)–Al(1)–N(2a) and Al(1)–N(2a)–Al(1a), respectively). The bond angle of the ethylaluminum fragment, Al(1)–C(6)–C(7), is 117.8 (7)°. The independent Al–Cl distances are 2.172 (3) and 2.163 (4) Å (for Al(2)–Cl(1) and Al(2)–Cl(2), respectively) while the Cl(1)–Al(2)–Cl(2) bond angle is 117.8 (8)°.

The title compound contains two $(C_2H_5)AlCl_2$ units. Therein lies the most striking feature of $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$: the absence of diethylaluminum chloride moieties. The presence of the $(C_2H_5)AlCl_2$ units may possibly be accounted for by the disproportionation of $[(C_2H_5)_2AlCl]_2$ to give $(C_2H_5)AlCl_2$ and $(C_2H_5)_3Al$. Indeed, dialkylaluminum halides have been shown to disproportionate in the presence of base to give alkylaluminum dihalides and trialkylaluminum.[34] Thus, it is quite reasonable that the disproportionation products resulted from a transient mixed alkyl–halo isomer (Figure 2) of the diethylaluminum chloride dimer. Transient existence of such a dimeric species for diethylaluminum chloride was initially suggested by Ziegler nearly 30 years ago.[35] Bridge cleavage of such a dimer would provide both $(C_2H_5)AlCl_2$ and $(C_2H_5)_3Al$ (Figure 2). The title compound could thus be obtained by the stronger Lewis acid, $(C_2H_5)AlCl_2$, preferentially forming adducts with two nitrogen atoms of the macrocycle. The remaining $(C_2H_5)_3Al$ species in solution is available to react, upon heating, with the N–H units along the macrocyclic cavity (resulting in the Al_2N_2 fragment). The overall reaction is given in eq 1.

$$2AlEt_3 + 2EtAlCl_2 + C_{10}H_{24}N_4 \rightarrow [AlEt]_2[C_{10}H_{20}N_4][AlEtCl_2]_2 + 4Et\text{–}H \quad (1)$$

The reaction of AlR_3 with macrocyclic amines possessing N–H units has been previously noted in this laboratory.[18–21] Characteristically, the products of such reactions possess Al_2N_2 fragments along the interior of the macrocyclic cavity that are isostructural with that of the title compound. Additionally, in all such reactions alkane is released. The isolation of the title compound has stimulated our interest in Al–N cage products, and studies are currently underway with regard to other organoaluminum species and multidentate amines.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554).

Registry No. $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$, 114221-38-4; $C_{10}H_{24}N_4$, 295-37-4; $(C_2H_5)_2AlCl$, 96-10-6.

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordintes, and thermal parameters (8 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Activation of a β-Lactone by Oxidative Addition and the Structure of a Platina(IV)lactone

Khin-Than Aye,[1a] Deanna Colpitts,[1a]
George Ferguson,*[,1b] and Richard J. Puddephatt*[,1a]

Department of Chemistry, University of Western Ontario
London, Ontario, Canada N6A 5B7, and
Department of Chemistry and Biochemistry
The University of Guelph
Guelph, Ontario, Canada N1G 2W1

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Summary: The oxidative addition of the CH_2–O bond of β-propiolactone to $[PtMe_2(NN)]$ (**1a**, NN = 2,2′-bipyridine; **1b**, NN = 1,10-phenanthroline) gives the corresponding platinalactone derivatives $[PtMe_2\{CH_2CH_2C(O)O\}(NN)]$ (**2a** and **2b**, respectively). The structure of **2b** has been determined crystallographically [space group *Pbca*; $a = 13.838$ (2), $b = 14.774$ (5), $c = 15.735$ (4) Å; $Z = 8$; $R = 0.035$ for 836 reflections]. Oxidative addition follows second-order kinetics, and the rate does not correlate with solvent polarity though the reaction is faster in hydroxylic solvents.

Metallalactones are probable intermediates in many transition-metal-catalyzed reactions involving formation of lactones or their derivatives and in the activation of lactones in organic synthesis,[2] but such complexes have

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(1) (a) University of Western Ontario. (b) University of Guelph.

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