Interaction of Trimethylaluminum and Trimethylgallium with the Acetate Ion. Synthesis and Crystal Structures of $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$ and $Rb[Ga_2(CH_3)_6CH_3COO]$

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Received December 30, 1981

The crystal structures of the closely related compounds $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$ and $Rb[Ga_2(CH_3)_6CH_3COO]$ have been determined from single-crystal X-ray diffraction data collected by counter methods. The former compound crystallizes in the orthorhombic space group *Pnma* with unit cell parameters a = 10.202 (3) Å, b = 10.300 (3) Å, c = 18.772 (5) Å, and ρ (calcd) = 0.93 g cm^{-3} for Z = 4, whereas the latter compound crystallizes in the triclinic space group $P\bar{1}$ with a = 8.986 (3) Å, b = 9.243 (3) Å, c = 9.281 (3) Å, α = 93.27 (4)°, β = 90.83 (4)°, γ = 103.61 (4)°, and ρ (calcd) = 1.66 g cm^{-3} for Z = 2. Least-squares refinement gave final R values of 0.086 and 0.077 for 973 and 2125 independent observed reflections, respectively. Both aluminum and gallium atoms are tetrahedrally coordinated, with M-O distances averaging 1.871 (4) Å for M = Al and 2.069 (1) Å for M = Ga and the corresponding M-C distances averaging 1.94 (2) and 2.00 (1) Å, respectively.

Introduction

The necessity to characterize related trimethylaluminum and trimethylgallium anionic adducts is important for two principle reasons. First, the phenomenon of liquid clathrates based upon aluminum alkyls, which was initially reported in 1972,[1] has been widely studied within our group in recent years, and it was soon realized that the geometry and size of the $[Al_2R_6X]^-$ anion has a considerable effect upon the nature of the liquid clathrate, notably the aromatic-to-anion ratio.[2] It would therefore be a natural extension to study the corresponding gallium-based liquid clathrates in terms of both solution behavior and solid-state structure. Second, only one other trialkylgallium adduct has been characterized crystallographically.[3] It was of interest to see if the structural changes between the trimethylaluminum and trimethylgallium adducts of the thiocyanate anion also carry over to other anions. We have therefore undertaken and herein report the synthesis and crystal structures of the closely related compounds rubidium bis(trimethylgallio)acetate and tetramethylammonium bis(trimethylalumino)acetate.

Experimental Section

Synthesis of $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$. $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$ was prepared by reacting 0.01 mol of $[N(CH_3)_4][CH_3COO]$ with 0.02 mol of $(CH_3)_3Al$ in excess *p*-xylene. Formation of the layering effect (liquid clathrate) characteristic of 2:1 complexes was noted immediately, and, as previously reported,[4,5] crystals of the 1:1 complex had formed within 30 min according to (1). Crystals of the 2:1 complex formed after the reaction mixture was left for a prolonged period of time (ca. 1 year in a sealed tube).

$$[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]\cdot\text{aromatic} \rightleftarrows [N(CH_3)_4][Al(CH_3)_3CH_3COO] + Al(CH_3)_3 + \text{aromatic} \quad (1)$$

Synthesis of $Rb[Ga_2(CH_3)_6CH_3COO]$. $Rb[Ga_2(CH_3)_6CH_3COO]$ was prepared in a similar manner with 0.002 mol of $Rb[CH_3COO]$ and 0.004 mol of $(CH_3)_3Ga$ being mixed in excess benzene at room temperature. Reaction was immediate, and a solution of the 2:1 complex was obtained with no layering effect having been observed. Crystals suitable for X-ray analysis were obtained directly via crystallization.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	$[N(CH_3)_4]$-$[Al_2(CH_3)_6$-$CH_3COO]$	$Rb[Ga_2(CH_3)_6$-$CH_3COO]$
mol wt	277.4	374.2
space group	*Pnma*	$P\bar{1}$
cell constants		
a, Å	10.202 (3)	8.986 (3)
b, Å	10.300 (3)	9.243 (3)
c, Å	18.772 (5)	9.281 (3)
α, deg		93.27 (4)
β, deg		90.83 (4)
γ, deg		103.61 (4)
cell vol, Å^3	1972.6	747.0
molecules/unit cell	4	2
ρ(calcd), gcm^{-3}	0.93	1.66
μ(calcd), cm^{-1}	1.46	66.43
radiatn	Mo Kα	Mo Kα
max cryst dimens, mm	0.35 × 0.45 × 1.25	0.10 × 0.35 × 0.40
scan width, deg	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
std reflctns	060, 004	400, 060, 003
decay of stds	...	...
reflctns measd	2117	2652
2θ range, deg	4-50	4-50
reflctns obsd ($I > 3\sigma(I)$)	975	2125
no. of parameters varied	84	118
GOF	1.70	2.02
R_1	0.086	0.077
R_2	0.089	0.081

X-ray Data Collection and Structure Solution for $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$. A single crystal of $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$ suitable for X-ray analysis was sealed in a thin-walled glass capillary prior to X-ray data collection. Final lattice parameters as determined from 15 high-angle reflections ($\theta > 20°$) carefully centered on an Enraf-Nonius CAD-4 diffractometer are given in Table I. Intensity data were collected on the diffractometer in a manner similar to that previously described.[6] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects but not for absorption (μ = 1.46 cm^{-1}). Systematic absences narrowed space group selection to either the

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Table II. Final Fractional Coordinates for $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$

atom	*x/a*	*y/b*	*z/c*
Al(1)	0.3937 (3)	0.7500	−0.0332 (2)
Al(2)	0.8210 (3)	0.7500	0.1700 (2)
O(1)	0.5580 (6)	0.7500	0.0114 (4)
O(2)	0.7162 (7)	0.7500	0.0884 (3)
N	−0.0895 (8)	0.7500	−0.1212 (4)
C(1)	0.598 (1)	0.7500	0.0755 (5)
C(2)	0.500 (1)	0.7500	0.1311 (6)
C(3)	0.437 (1)	0.7500	−0.1334 (7)
C(4)	0.3036 (8)	0.9086 (7)	−0.0019 (5)
C(5)	0.996 (1)	0.7500	0.1318 (6)
C(6)	0.7789 (9)	0.5894 (8)	0.2204 (4)
C(7)[a]	0.027 (3)	0.7500	−0.160 (2)
C(7)′	−0.016 (5)	0.643 (5)	−0.156 (3)
C(8)	−0.093 (4)	0.7500	−0.047 (2)
C(8)′	−0.072 (4)	0.648 (5)	−0.070 (2)
C(9)	−0.179 (5)	0.862 (5)	−0.148 (2)
C(9)′	−0.201 (6)	0.7500	−0.150 (3)
H(1)[C(2)]	0.404	0.750	0.113
H(2)[C(2)]	0.523	0.814	0.163
H(3)[C(3)]	0.359	0.750	−0.177
H(4)[C(3)]	0.498	0.835	−0.150
H(5)[C(4)]	0.229	0.894	0.044
H(6)[C(4)]	0.265	0.952	−0.038
H(7)[C(4)]	0.364	0.961	0.020
H(8)[C(5)]	1.060	0.750	0.174
H(9)[C(5)]	1.002	0.828	0.098
H(10)[C(6)]	0.752	0.513	0.199
H(11)[C(6)]	0.703	0.592	0.250
H(12)[C(6)]	0.845	0.568	0.246

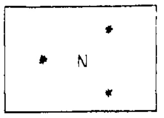
[a] Carbon atoms of the disordered cation have occupancy factors of 0.333.

centrosymmetric *Pnma* or noncentrosymmetric $Pn2_1a$. *Pnma* was initially chosen and was shown to be correct by the successful refinement of the data.

Table III. Final Fractional Coordinates for $Rb[Ga_2(CH_3)_6CH_3COO]$

atom	*x/a*	*y/b*	*z/c*
Rb	0.4902 (2)	0.7037 (2)	0.6158 (1)
Ga(1)	0.5746 (2)	0.7420 (1)	0.2024 (1)
Ga(2)	0.0346 (2)	0.2160 (2)	0.2860 (2)
O(1)	0.418 (1)	0.5839 (9)	0.3066 (9)
O(2)	0.2329 (9)	0.3833 (9)	0.316 (1)
C(1)	0.516 (2)	0.720 (2)	−0.007 (1)
C(2)	0.757 (2)	0.668 (2)	0.263 (2)
C(3)	0.543 (2)	0.933 (2)	0.298 (2)
C(4)	−0.100 (2)	0.292 (2)	0.427 (2)
C(5)	0.132 (2)	0.055 (2)	0.343 (2)
C(6)	−0.018 (3)	0.211 (2)	0.076 (2)
C(7)	0.282 (1)	0.515 (1)	0.276 (1)
C(8)	0.178 (2)	0.587 (2)	0.187 (2)

The structure was solved by application of the direct methods program MULTAN.[7] Inspection of a difference Fourier map based on all non-hydrogen atoms excluding the carbon atoms of the cation revealed disorder of the tetramethylammonium ion. Peaks corresponding to carbon atoms were found on and off the mirror plane for each carbon position. If no disorder were present, there would be two independent carbon atoms in the mirror plane and one off. Instead, three peaks were found in the mirror plane (**2**) and three above and three below (**3**), all with approximately the same height. This can be accounted for with reference to equal contributions from **4**–**6**. Therefore each carbon atom out of the mirror plane is in fact present one-third of the time (fraction × multiplicity) = occupancy factor: (1/3)(1) = 0.333), and each carbon atom on the mirror is actually present two-thirds of the time (2/3)(0.5) = 0.333). Occupancy factors for each of the six disordered positions were assigned as 0.333. Refinement in the noncentrosymmetric space group, $Pn2_1a$, resulted in a higher R factor and high correlations between the parameters of the anion not in the plane. Several cycles of refinement of the positional and isotropic thermal parameters of the non-hydrogen atoms afforded a reliability index of $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.121$. Conversion to anisotropic thermal parameters and further refinement gave $R_1 = 0.090$. The hydrogen atom positions of the anion were determined from a difference Fourier map and were not refined. More cycles of refinement led to final values of $R_1 = 0.086$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2\}^{1/2} = 0.089$. The largest parameter shifts in the final cycle of refinement were less than 0.1 of their estimated standard deviations for the anion and the nitrogen atom. The final difference Fourier showed no feature greater than 0.4 e/Å^3. The standard deviation of an observation of unit weight was 1.70. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The function $w(|F_o| - |F_c|)^2$ was minimized.[7] Neutral atom scattering factors were taken from the compilations of Cromer and Waber[8] for Al, N, and C. No corrections were made for anomalous dispersion.[9] Scattering factors for H were taken from ref 10. The final fractional coordinates are given in Table II. The final values of the thermal parameters are given in the supplementary material.[11]



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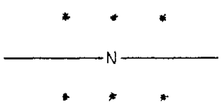

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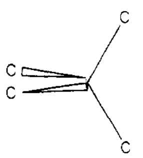

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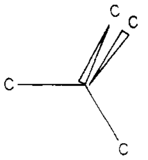

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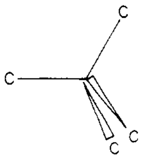

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X-ray Data Collection and Structure Solution for $Rb[Ga_2(CH_3)_6CH_3COO]$. A single, platelike crystal of the colorless, air-sensitive compound was sealed in a thin-walled capillary. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($\theta > 15°$) accurately centered on the diffractometer are given in Table I. The data collection procedures were identical with those of $[N(CH_3)_4][Al_2(CH_3)_6COO]$ (Table I). The structure was solved by application of MULTAN and, after correction for absorption, was refined to final values of $R_1 = 0.074$ and $R_2 = 0.081$. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms could not be located. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. The final fractional coordinates are given in Table III. The final values of the thermal parameters are given in the supplementary material.[11]

Discussion

The structures and atom numbering schemes of the $[M_2(CH_3)_6CH_3COO]^-$ anions are presented in Figure 1. The anion for M = Al lies on a crystallographic mirror plane containing Al(1), Al(2), O(1), O(2), C(1), C(2), C(3), and C(5). The two independent Al atoms are tetrahedrally coordinated with Al–C distances ranging from 1.93(1) to 1.965(8) Å (Table IV). Table V, which gives a survey of related distances, shows that the aforementioned bond

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(7) By G. Germain, P. Main, and M. M. Woolfson. Other crystallographic programs used on a UNIVAC 1110 include ORFFE (distances and angles with esd's, by W. R. Busing, K. O. Martin, and H. A. Levy), FOURIER (Fourier synthesis, D. J. Hodgon's version of Dellaca and Robinson's program), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), and SHELX (Fourier synthesis and least-squares refinement, by G. Sheldrick).

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(9) Cromer, D. T.; Liberman, J. T. *J. Chem. Phys.* **1970**, *53*, 1891.

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(11) See paragraph at the end of paper regarding supplementary material.

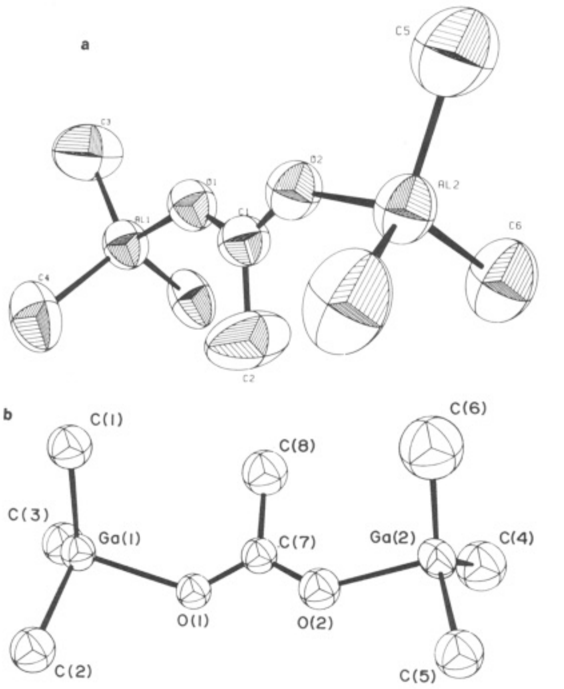

Figure 1. Structure of the $[M_2(CH_3)_6CH_3COO]^-$ anions with the atoms represented by their 50% probability ellipsoids for thermal motion: (a) M = Al; (b) M = Ga.

Table IV. Bond Lengths (Å) and Bond Angles (Deg) for $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$

	Bond Lengths		
Al(1)-O(1)	1.874 (7)	Al(2)-O(2)	1.868 (8)
Al(1)-C(3)	1.93 (1)	Al(2)-C(5)	1.93 (1)
Al(1)-C(4)	1.965 (8)	Al(2)-C(6)	1.953 (8)
C(1)-O(1)	1.27 (1)	C(1)-O(2)	1.23 (1)
C(1)-C(2)	1.44 (2)		
N-C(7)′	1.49 (5)	N-C(7)	1.39 (3)
N-C(8)′	1.43 (5)	N-C(8)	1.40 (4)
N-C(9)′	1.26 (6)	N-C(9)	1.55 (5)
	Bond Angles		
O(1)-Al(1)-C(3)	103.4 (5)	O(2)-Al(2)-C(5)	103.1 (4)
O(1)-Al(1)-C(4)	106.6 (3)	O(2)-Al(2)-C(6)	105.7 (3)
C(3)-Al(1)-C(4)	113.5 (3)	C(5)-Al(2)-C(6)	112.6 (3)
C(4)-Al(1)-C(4)[a]	112.5 (5)	C(6)-Al(2)-C(6)[a]	115.8 (5)
Al(1)-O(1)-C(1)	135.1 (7)	Al(2)-O(2)-C(1)	136.3 (7)
O(1)-C(1)-O(2)	119.9 (9)	O(1)-C(1)-C(2)	118 (1)
O(2)-C(1)-C(2)	122 (1)	C(7)-N-C(8)	123 (2)
C(7)-N-C(9)	110 (2)	C(8)-N-C(9)	108 (2)
C(7)′-N-C(9)[a]	96 (3)	C(7)′-N-C(8)′	141 (3)
C(7)′-N-C(9)′	106 (3)	C(8)′-N-C(9)′	114 (2)
C(7)′-N-C(7)′[a]	96 (4)	C(8)′-N-C(8)′[a]	94 (4)

[a] Atoms related to those in Table II by (x, $^3/_2 - y$, z).

lengths are typical for a compound of this type. The Al–O distances of 1.874 (7) and 1.868 (8) Å are also within the previously observed range[4,12–14] and are, as might be expected, longer than the 1.83 (1) Å observed for the 1:1 adduct.[5] Bond angles around the aluminum atoms are consistent with a slightly distorted sp^3-hybridized tetrahedron, and the angles and distances within the rest of the anion are consistent with the type of delocalized bonding observed in organic acetates.

The bond lengths and angles associated with the tetramethylammonium cation have large esd's because of the disorder, but the closest approach of the anion to the nitrogen atom of the cation is greater than 3.5 Å. A stereoscopic view of the cell packing is given in Figure 2.

Table V. Comparison of Aluminum–Carbon and Aluminum–Oxygen Distances (Å) in Adducts Which Contain $(CH_3)_3Al–O$ Linkages

compd	Al–C	Al–O	ref
$[N(CH_3)_4][Al(CH_3)_3\text{-}CH_3COO]$	2.02 (2)	1.83 (1)	5
$[K\cdot DB\text{-}18\text{-}C\text{-}6][Al_2(CH_3)_6\text{-}O_2]\cdot 1.5benzene$[a]	1.97 (1)	1.85 (1) 1.87 (1)	12
$[N(CH_3)_4][Al_2(CH_3)_6\text{-}CH_3COO]$	1.95 (2)	1.868 (8) 1.874 (7)	this study
$K_2[Al_4(CH_3)_{12}SO_4]\cdot 0.5p$-xylene	1.96 (3)	1.886 (9) 1.889 (9) 1.89 (1) 1.977 (9)	13
$[K\cdot DB\text{-}18\text{-}C\text{-}6][Al(CH_3)_3\text{-}NO_3]\cdot 0.5benzene$	1.96 (1)	1.92 (1)	14
$K[Al(CH_3)_3NO_3]$	1.97 (1)	1.930 (6)	4
$K[Al_2(CH_3)_6NO_3]$	1.99 (6)	1.95 (5) 2.01 (5)	4

[a] DB-18-C-6 = dibenzo-18-crown-6.

Table VI. Comparison of Gallium–Carbon and Gallium–Oxygen Distances (Å) in Adducts Related to the Title Compounds

compd	Ga–C	Ga–O	ref
$CH_3Ga(CH_3COO)_2$	1.946 (3)	1.873 (3) 2.086 (3)	15
$[(CH_3)_2NCH_2CH_2OGaH_2]_2$		1.911 (3) 2.053 (3)	16
$[(CH_3)_2NCH_2CH_2OGa\text{-}(CH_3)_2]_2$	1.961 (4)	1.913 (3) 2.078 (3)	16
$[C_7H_5O_2\cdot Ga(CH_3)_2]_2$	1.939 (1)	1.927 (3) 2.120 (3)	17
$Ga(CH_3COO)_3$		1.941 (7) 1.964 (6)	18
$[CH_3N(CH_2CH_2O)_2GaH]_2$		1.960 (8) 2.018 (2)	19
$[(CH_3)_2Ga]_2C_2O_4$	1.941 (5)	2.051 (7) 2.124 (9)	20
$Rb[Ga_2(CH_3)_6CH_3COO]$	2.00 (1)	2.068 (8) 2.070 (8)	this study

The anion for M = Ga has the same overall geometry as its aluminum-based counterpart; this is important since both are therefore different in conformation to the $[Al_2(CH_3)_6NO_3]^-$ anion.[4] (The reasons for this are discussed subsequently at a later part of this paper.) The only major difference may be seen with regard to the metal atom placement relative to the plane of the acetate ion. For the trimethylaluminum complex, the two Al atoms lie in the crystallographic mirror plane which contains the acetate group. For the trimethylgallium complex, Ga(1) and Ga(2) lie 0.78 and 0.13 Å, respectively, out of the acetate plane. (Both are on the same side of the plane.)

The Ga–O distances of 2.068 (8) and 2.070 (8) Å and the Ga–C distances of 1.98 (2)–2.01 (1) Å are compared with related organogallium compounds in Table VI. They are amongst the longest yet observed,[15–20] but they are on the same order as those in $[(CH_3)_2Ga]_2C_2O_4$,[20] which is perhaps the nearest analogue amongst previously determined organogallium–oxygen moieties. The other bond distances

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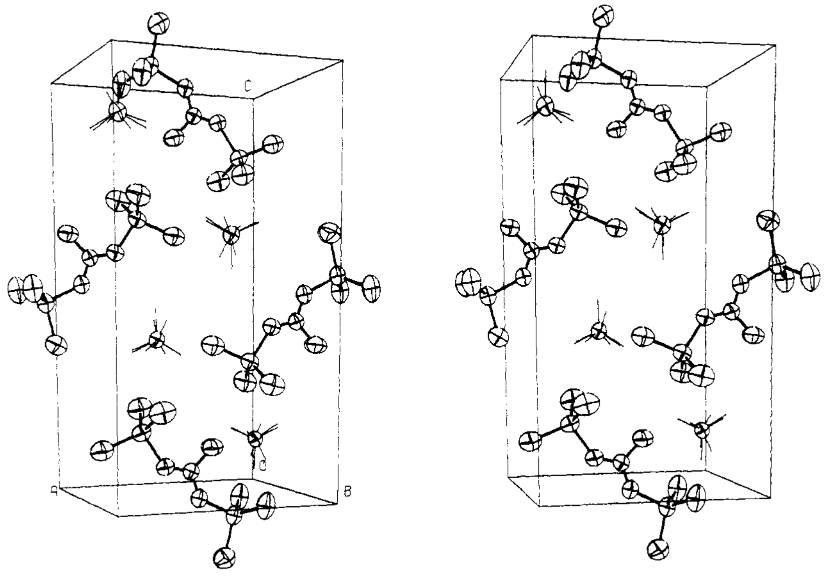

Figure 2. Stereoscopic view of the cell packing for $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$ with the disordered cations represented by the line bonds to the carbon atom positions.

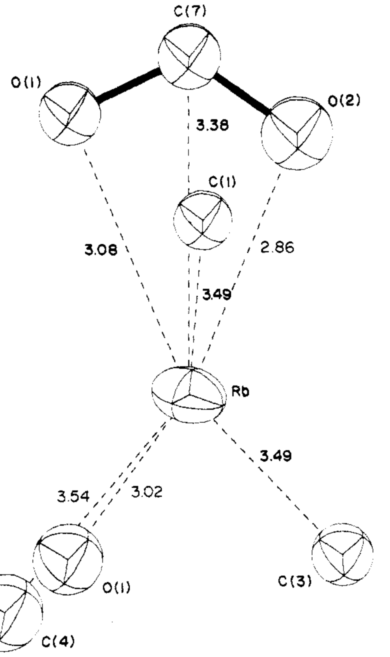

Figure 3. Cation environment in $Rb[Ga_2(CH_3)_6CH_3COO]$.

and angles, as given in Table VII, are consistent with the same hybridization scheme as that for the aluminum analogue.

The closest contacts to the rubidium cation are 2.861 (4) and 3.021 (4) Å and arise from the oxygen atoms of the acetate. A view of the cation environment is given in Figure 3, and a stereoscopic view of the cell packing is given in Figure 4.

Table VII. Bond Lengths (Å) and Angles (Deg) for $Rb[Ga_2(CH_3)_6CH_3COO]$

Bond Lengths			
Ga(1)-O(1)	2.068 (8)	Ga(2)-O(2)	2.070 (8)
Ga(1)-C(1)	1.99 (1)	Ga(2)-C(4)	2.00 (2)
Ga(1)-C(2)	2.00 (2)	Ga(2)-C(5)	1.98 (2)
Ga(1)-C(3)	2.01 (1)	Ga(2)-C(6)	1.99 (2)
O(1)-C(7)	1.26 (1)	O(2)-C(7)	1.27 (1)
C(7)-C(8)	1.53 (2)		
Bond Angles			
O(1)-Ga(1)-C(1)	108.0 (5)	O(2)-Ga(2)-C(4)	99.9 (6)
O(1)-Ga(1)-C(2)	94.8 (5)	O(2)-Ga(2)-C(5)	94.6 (5)
O(1)-Ga(1)-C(3)	101.7 (5)	O(2)-Ga(2)-C(6)	104.6 (7)
C(1)-Ga(1)-C(2)	117.5 (7)	C(4)-Ga(2)-C(5)	118.5 (8)
C(1)-Ga(1)-C(3)	112.2 (6)	C(4)-Ga(2)-C(6)	118.3 (10)
C(2)-Ga(1)-C(3)	118.9 (7)	C(5)-Ga(2)-C(6)	114.8 (9)
C(7)-O(1)-Ga(1)	132.9 (8)	C(7)-O(2)-Ga(2)	136.6 (8)
O(1)-C(7)-O(2)	119.7 (11)	O(2)-C(7)-C(8)	120.1 (11)
O(1)-C(7)-C(8)	120.2 (11)		

The conformations that are possible for anions of this nature are given schematically in Figure 5: the title compounds fall into category A. It is evident that type C is precluded because of the steric interactions that would prevail amongst the $M(CH_3)_3$ units: however, it is not obvious immediately why the B conformation is not found, since it would minimize $M(CH_3)_3$-methyl(acetate) steric repulsions and it is also the type preferred by the related $[Al_2(CH_3)_6NO_3]^-$ anion.[4]

It is believed that A is favored primarily due to packing considerations, particularly after noting the relatively close

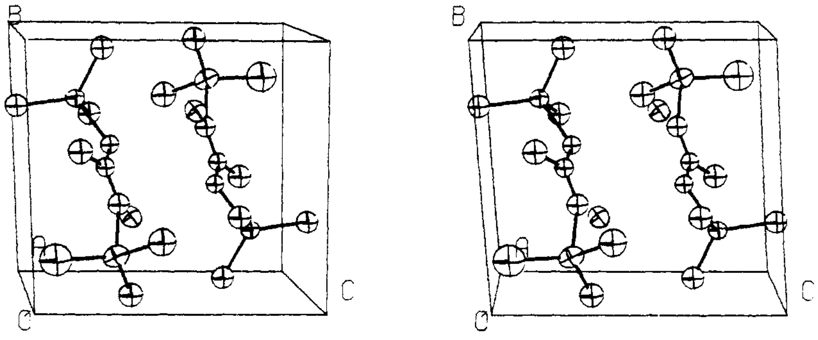

Figure 4. Stereoscopic view of the unit cell packing for $Rb[Ga_2(CH_3)_6CH_3COO]$.

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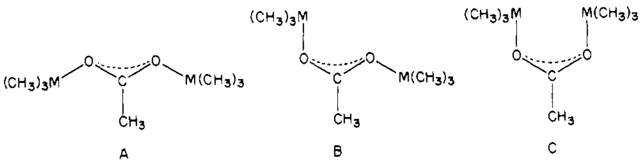

Figure 5. Possible conformations for the $[M_2(CH_3)_6CH_3COO]^-$ anions.

Table VIII. Comparison of Distances (Å) within the $(CH_3)_3M$-O Unit

	M		
	Al	Ga	increase
M-O(av)	1.871 (4)	2.069 (1)	0.20
M-C(av)	1.94 (2)	2.00 (1)	0.06
covalent radius[a] M^{3+}	0.50	0.62	0.12

[a] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; 4th ed.; Interscience: New York, 1980; p 14.

Rb–O nonbonded interactions in the gallium analogue. Evidence of a small degree of strain in the anions is manifested by the wide C–O–M angles of 135.1 (7) and 136.3 (7)° for the aluminum and 132.9 (8) and 136.6 (8)° for the gallium derivatives. The corresponding angle in $[Al_2(CH_3)_6NO_3]^-$ is 129 (5)°. The possibility that the driving force could be the greater delocalization in A over that in B cannot be ruled out.

Another feature of interest in the anions is the relative M–O and M–C distances. As can be seen from Table VIII a bond lengthening on the order of 0.12 Å as one progresses from Al to Ga might be expected on the basis of ionic radii. In fact, however, it is seen that the M–O distances show a larger than expected increase of 0.20 Å and that the M–C distances give a considerably smaller increase of 0.06 Å. A similar effect is seen in the M–N distances in the $[M(CH_3)_3NCS]^-$ anions.[3] Clearly the group 3 congeners exhibit different bonding patterns which cannot easily be predicted. Further comparative studies are therefore in order.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$, 81432-62-4; $Rb[Ga_2(CH_3)_6CH_3COO]$, 82456-38-0.

Supplementary Material Available: Thermal parameters and observed and calculated structure factors for both compounds (22 pages). Ordering information is given on any current masthead page.

A β-Elimination Reaction Involving a Binuclear Ethylplatinum(II) Complex

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Received April 6, 1982

The new ethylplatinum complexes $[PtEt_2(dppm)]$, $[PtClEt(dppm)]$, $[Pt_2Et_2(\mu\text{-}H)(\mu\text{-}dppm)_2][SbF_6]$ (IIb), and $[Pt_2Et_3(\mu\text{-}dppm)_2][SbF_6]$ (Ib) have been prepared and characterized (dppm = $Ph_2PCH_2PPh_2$). Of particular interest is the facile reaction of Ib to give IIb and ethylene in solution, which is formally a binuclear β-elimination process. Reaction of $[Pt(CH_2CD_3)_2(dppm)]$ with $H[SbF_6]$ gave the analogue of Ib in which scrambling of H and D within the ethyl groups had occurred, while thermolysis of a mixture of Ib and $[Pt_2(CD_2CD_3)_3(\mu\text{-}dppm)_2][SbF_6]$ (Ic) gave C_2H_4 and C_2D_4 as volatile products. Thermolysis of Ib in 1,2-dichloroethane, acetone, or acetonitrile followed first-order kinetics, and the reaction was not retarded by added dppm. From consideration of the Arrhenius parameters for thermolysis of Ib and from the low isotope effect on the rate of thermolysis of Ic, it is argued that neither the β elimination nor the ethylene dissociation step is rate-determining in the thermolysis of Ib.

Introduction

Platinum metal is an important catalyst, for example, in alkene hydrogenation, and efforts have been made to model reactions proposed to occur in such catalysis by study of discrete platinum complexes. The insertion of ethylene into a Pt–H bond or the reverse β elimination of ethylene from an ethylplatinum group have been studied in great detail in mononuclear platinum complexes.[2-4] Binuclear platinum complexes should be better models (although still highly imperfect) for a platinum surface, since it is then at least possible that cooperative effects involving both platinum atoms may be involved in the organometallic reactions, as is often proposed to occur in surface catalysis.[5] However, no reactions of alkenes with binuclear platinum hydrides or β-elimination reactions from binuclear alkylplatinum complexes have been reported.[6,7] In this article a new triethyldiplatinum(II) complex cation, $[Pt_2Et_3(\mu\text{-}dppm)_2]^+$ (dppm =

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