Arene complexes of zirconium containing triangular cluster cations $[(\eta^6\text{-}C_6H_6Me_3)_3Zr_3(\mu\text{-}Cl)_6]^{n+}$, $n = 2,3$

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Ionic π-mesitylene zirconium complexes (**1—4**) have been obtained by a reaction between $ZrCl_4$ and a metal reducer (Al, Zn or Mg) in the presence of $AlCl_3$ in mesitylene. An X-ray study has shown that in the triangular cluster cations $[(\eta^6\text{-}C_6H_3Me_3)_3Zr_3(\mu\text{-}Cl_6)]^{n+}$ an increase in the charge from 2+ (**1,2**) to 3+ (**3,4**) is accompanied by shortening of the Zr—Zr distances from 3.32—3.33 Å to 3.27—3.28 Å. $AlCl_4^-$ (**1**), $Al_2Cl_7^-$ (**1—3**), and $Mg[(\mu\text{-}Cl)_2AlCl_2]_3^-$ (**4**), the latter found here for the first time, are present in the complexes studied as counterions.

Key words: zirconium, arene complexes, triangular clusters.

In the wake of the discovery of the first bis-arene complexes of chromium there were some attempts to synthesize similar compounds for most of the other transition metals, among them Ti and Zr. In the pioneer work of E. O. Fischer and coworkers,[1] the reductive Friedel-Crafts reaction was used to synthesize bis-arene complexes of titanium and zirconium. Actually they isolated cationic complexes which, based on electroconductivity (Ti) and magnetic susceptibility (Ti, Zr) studies, were assigned the formula $[(C_6Me_6)_3M_3Cl_6]Cl$ (**5**) which includes single-charged trinuclear cations. In attempting to reproduce this synthesis for the zirconium system (however, under slightly different conditions) a $[(C_6Me_6)_3Zr_3Cl_6](Al_2Cl_7)_2$ crystal complex (**6**) that contained doubly-charged cluster cations[2] was isolated.

The further study of similar systems with other halogenides, bromide and iodide, revealed the diversity of the possible complexes with compositions dependent both on the halogen type and on the arene ligand used. Thus, in the bromide system (Arene = benzene) at the first stages of reduction a Zr(III) complex with the dimeric structure $\{(\mu\text{-}Br)_3[(\eta^6\text{-}C_6H_6)Zr(\mu\text{-}Br)_2AlBr_2]_2\}(Al_2Br_7)\ 2.5C_6H_6$ (**7**) is formed.[3] At the same time, in the iodide system under similar conditions the reduction proceeds farther and a Zr(II) complex, $[(\eta^6\text{-}C_6H_6)_2Zr(\mu\text{-}I)_2AlI_2](Al_3I_{10})0.5C_6H_6$ (**8**), is isolated.[3] Zirconium (II) complexes containing cations of the analogous structure were isolated in the bromide system as well, but in the case when Arene = mesitylene.[4]

The results of the investigation of the aromatic complexes of zirconium (and hafnium) synthesized in a similar way are given in Refs. 5, 6. Based on the data of chemical analysis and spectroscopy in the UV- and visible light regions, the authors suggested the $(\eta^6\text{-Arene})Zr[(\mu\text{-}X)_2AlX_2]_2$ formula for the Zr(II) complexes, taking into consideration the close chemical analogy between titanium and zirconium. However, the absence of crystal products did not allow the authors[5,6] to give an unequivocal interpretation of the experimental data.

The present work is devoted to the synthesis and study of mesitylene complexes of zirconium forming in a chloride system. The isolation and X-ray study of crystals of four complexes allowed us to establish the possibility of the existence of trinuclear cluster cations: $[(\eta^6\text{-}C_6H_3Me_3)_3Zr_3Cl_6)]^{n+}$ with charge 2 or 3. It is significant that alteration of the charge produces a considerable effect on the Zr—Zr distances in the triangular clusters.

Results and Discussion

Ionic complexes **1—4** (Table 1) are formed in the interaction of $ZrCl_4$ in the presence of $AlCl_3$ with metal reducers Al or Mg under different conditions in a mesitylene medium. X-Ray analysis study has shown all the complexes to consist of a trinuclear cluster cation $[(\eta^6\text{-}C_6H_3Me_3)_3Zr_3(\mu\text{-}Cl)_6]^{n+}$ and the respective number of haloaluminate anions: $n = 2$, $AlCl_4^-$, $Al_2Cl_7^-$ (complex **1**); $n = 2$, $2(Al_2Cl_7^-)$ (**2**); $n = 3$, $3(Al_2Cl_7^-)$ (**3**); $n = 3$, $3[Mg(AlCl_4)_3]^-$ (**4**). The geometric structure of a cluster ion, which is similar for all complexes **1—4**, is shown in Fig. 1. The main differences are in the Zr—Zr distances for $n = 2$ or 3 (see below) and in the orientation of the mesitylene ligands towards the cluster triangle plane. While the formation of complexes with single-charge trinuclear cations in the systems in question has

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Table 1. Crystal characteristics of complexes **1—4**

Parameter	Compound			
	1	**2**	**3**	**4**
	$[(\eta^6\text{-}C_6H_3Me_3)_3Zr_3(\mu\text{-}Cl)_6]^{n+}$			
	$n = 2$	$n = 2$	$n = 3$	$n = 3$
	$AlCl_4^-$, $Al_2Cl_7^-$	$(Al_2Cl_7)_2^-$	$(Al_2Cl_7)_3^-$	$[Mg(AlCl_4)_3]_3^-$
Space group	$Pna2_1$	$P2_1/n$	$Pca2_1$	$R3H$
a/Å	17.157(5)	15.776(5)	49.556(9)	17.501(4)
b/Å	13.311(3)	14.865(7)	14.367(3)	
c/Å	21.875(4)	23.609(5)	18.790(4)	51.494(15)
β/deg		96.58(2)		
V/Å^3	4995.7	5500.1	13378	13659
Z	4	4	8	6
d_{calc}/g cm^{-3}	1.752	1.752	1.741	1.779
μ(Mo)/cm^{-1}	15.98	16.23	16.44	17.10
θ_{max}/deg	26	23	20	21
N_1*	5437	6289	6932	4204
N_2	3595	3242	2848	1765
(p)	(3)	(3)	(3)	(2)
N_3	450	370	342	318
R	0.052	0.105	0.112	0.075
R_w	0.056	0.113	0.121	0.079

Note. N_1 is the number of the measured reflexes; N_2 is the number of the reflexes in the least-squares with $I > p\,\sigma(I)$; N_3 is the number of the variables in the least-squares.

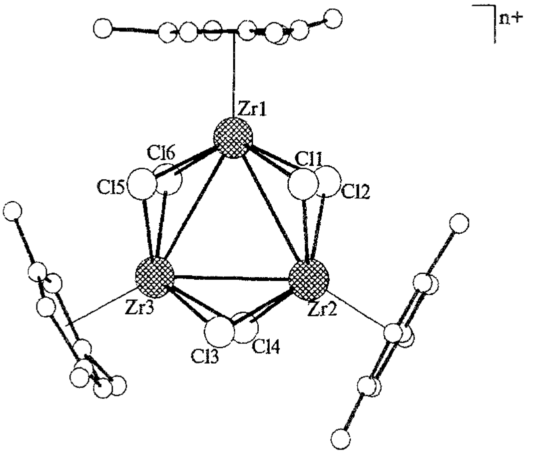

Fig. 1. The structure of triangular cluster cations $[\eta\text{-}C_6H_3Me_3)_3Zr_3(\mu\text{-}Cl)_6]^{n+}$ in structures **1—4**.

been postulated based on physico-chemical properties,[1] and double-charge complex cations of this type have been discovered previously (Arene = hexametylbenzene, HMB),[2,5] the possibility of the existence of triple-charged cluster cations was established here for the first time.

The reductive Friedel-Crafts synthesis is widely used to synthesize aromatic complexes of transition metals. If this reaction is used for preparing Ti and Zr complexes, the interaction is represented by the scheme:

$$MX_4 + AlX_3 + M' + \text{Arene} \rightarrow M(\text{II-III})\ \text{complex}$$

The composition and structure of the complexes of titanium and zirconium formed differ appreciably due to the different atomic sizes and, consequently, their coordination possibilities and the most stable electron configuration of the valence shell. The compositions of most of the arene complexes of titanium correspond to the formulas $(\eta^6\text{-Arene})_2Ti$ or $(\eta^6\text{-Arene})Ti[(\mu\text{-}X)_2AlX_2]$, where the Ti atom has a sixteen-electron valence shell.[7—11]

Unlike this, the composition and structure of the zirconium complexes depend on several factors, the main of which are the nature of the halide ligand X (Cl, Br, I), the metal reducer M, the arene ligand $C_6H_{6-m}Me_m$, and the $MX_4 : AlX_3$ ratio, as well as the duration and other conditions of the interaction. Very often a mixture of several products results at the end of the reaction. If their solubility in the excess arene ligand is not very high, a distinct oil-like phase is separated. Crystallizing products from this oil-like phase is extremely difficult. It can be stated that, for systems with one and the same arene ligand, the extent of zirconium reduction with a given metal (the most complete data are for M = Al) increases in the senes Cl < Br < I. For example, in benzene systems for X = Cl the reduction of aluminum proceeds very slowly even with heating (crystal complexes were not isolated); Zr(III) bromide complexes are formed already at room temperature, while the use of iodides leads to Zr(II) complexes at once.[3] At the same time, even without changing the type of arene ligand and halogen, it is possible to synthesize zirconium complexes with a formal oxidation degree from 3 to 2 by varying the quantity of the metal reducer and the duration of the interaction. Thus, for the system with Arene = mesitylene, X = Cl and M = Al, Zr complexes with oxidation degree 3.0 (**3**), 2.667 (**1**, **2**) and 2.0 in the case of $(\eta^6\text{-MeS})Zr(AlCl_4)_2$,[5] were obtained, although for the latter, the oxidation degree of Zr could be established reliably, but not the complex structure.

The present work shows for the first time that complexes with an analogous structure can be obtained when using not only Al but also less active metals, Mg or Zn, as metal reducers. Due to their lower activity, the reduction stops at Zr(III). This is confirmed, in particular, by the formation of one and the same crystal complex **4** both at the beginning of the interaction (3—4 hours at room temperature) and after heating the reaction mixture for 4—5 days at 100°C. According to preliminary data, complex **3** can be obtained not only at the initial stages of reduction with aluminum but also in a continuous reaction with metallic Zn.

There is one more factor leading to a variety of complexes in the same system, *i.e.*, the concentration of excess AlX_3 affecting the composition of the anions. Most often $Al_2X_7^-$ are present as haloaluminate anions: $Al_2Cl_7^-$ in complexes **1—3**, **6** and $Al_2Br_7^-$ in complex **7**. A reduced concentration of AlX_3 in the solution leads to

Table 2. Interatomic distances (Å) in structures **1**–**4**

Distance	*d*	Distance	*d*
***Complex* 1**			
Zr(1)—Zr(2)	3.320(2)	Zr(1)—C(average)	2.58
Zr(1)—Zr(3)	3.342(2)	Zr(2)—C(average)	2.62
Zr(2)—Zr(3)	3.333(2)	Zr(3)—C(average)	2.60
Zr(1)—Cl(1)	2.555(3)	Al(1)—Cl(7)	2.108(7)
Zr(1)—Cl(2)	2.548(4)	Al(1)—Cl(8)	2.087(8)
Zr(1)—Cl(5)	2.549(4)	Al(1)—Cl(9)	2.092(8)
Zr(1)—Cl(6)	2.554(3)	Al(1)—Cl(10)	2.262(8)
Zr(2)—Cl(1)	2.518(3)	Al(2)—Cl(10)	2.272(7)
Zr(2)—Cl(2)	2.521(4)	Al(2)—Cl(11)	2.081(7)
Zr(2)—Cl(3)	2.539(3)	Al(2)—Cl(12)	2.095(7)
Zr(2)—Cl(4)	2.541(3)	Al(2)—Cl(13)	2.099(7)
Zr(3)—Cl(3)	2.542(3)	Al(3)—Cl(14)	2.107(7)
Zr(3)—Cl(4)	2.552(4)	Al(3)—Cl(15)	2.115(9)
Zr(3)—Cl(5)	2.537(4)	Al(3)—Cl(16)	2.133(9)
Zr(3)—Cl(6)	2.556(4)	Al(3)—Cl(17)	2.07(1)
Complex* 2			
Zr(1)—Zr(2)	3.322(4)	Zr(3)—Cl(5)	2.523(9)
Zr(1)—Zr(3)	3.320(4)	Zr(3)—Cl(6)	2.554(10)
Zr(2)—Zr(3)	3.327(5)	Zr(1)—C(average)	2.57
Zr(1)—Cl(1)	2.542(9)	Zr(2)—C(average)	2.59
Zr(1)—Cl(2)	2.522(10)	Zr(3)—C(average)	2.60
Zr(1)—Cl(5)	2.544(9)	Al(1)—Cl(7)	2.07(2)
Zr(1)—Cl(6)	2.530(10)	Al(1)—Cl(8)	2.07(2)
Zr(2)—Cl(1)	2.539(8)	Al(1)—Cl(9)	2.10(1)
Zr(2)—Cl(2)	2.540(9)	Al(1)—Cl(10)	2.29(2)
Zr(2)—Cl(3)	2.536(9)	Al(2)—Cl(10)	2.27(2)
Zr(2)—Cl(4)	2.533(10)	Al(2)—Cl(11)	2.08(2)
Zr(3)—Cl(3)	2.545(9)	Al(2)—Cl(12)	2.05(1)
Zr(3)—Cl(4)	2.550(10)	Al(2)—Cl(13)	2.10(2)
***Complex* 3**			
Zr(1)—Zr(2)	3.30(1)	Zr(4)—Zr(5)	3.26(1)
Zr(1)—Zr(3)	3.26(1)	Zr(4)—Zr(6)	3.28(1)
Zr(2)—Zr(3)	3.29(1)	Zr(5)—Zr(6)	3.25(1)
Zr(1)—Cl(average)	2.50	Zr(4)—Cl(average)	2.54
Zr(2)—Cl(average)	2.55	Zr(5)—Cl(average)	2.50
Zr(3)—Cl(average)	2.50	Zr(6)—Cl(average)	2.53
Zr(1)—C(average)	2.58	Zr(4)—C(average)	2.61
Zr(2)—C(average)	2.61	Zr(5)—C(average)	2.63
Zr(3)—C(average)	2.61	Zr(6)—C(average)	2.62
***Complex* 4**			
Zr(1)—Zr(1')	3.284(7)	Zr(2)—Zr(2')	3.274(5)
Zr(1)—Cl(1)	2.54(1)	Zr(2)—Cl(3)	2.56(1)
Zr(1)—Cl(1')	2.53(1)	Zr(2)—Cl(3')	2.51(1)
Zr(1)—Cl(2)	2.50(1)	Zr(2)—Cl(4)	2.50(1)
Zr(1)—Cl(2')	2.51(1)	Zr(2)—Cl(4')	2.50(1)
Zr(1)—C(average)	2.61	Zr(2)—C(average)	2.61
Mg(1)—Cl(5)	2.47(2)	Mg(4)—Cl(17)	2.44(2)
Mg(1)—Cl(6)	2.54(2)	Mg(4)—Cl(18)	2.56(2)
Al(1)—Cl(5)	2.18(2)	Al(4)—Cl(17)	2.19(2)
Al(1)—Cl(6)	2.18(2)	Al(4)—Cl(18)	2.16(2)
Al(1)—Cl(7)	2.13(2)	Al(4)—Cl(19)	2.06(3)
Al(1)—Cl(8)	2.07(3)	Al(4)—Cl(20)	2.08(3)
Mg(2)—Cl(9)	2.51(2)	Mg(5)—Cl(21)	2.49(2)
Mg(2)—Cl(10)	2.50(2)	Mg(5)—Cl(22)	2.48(2)
Al(2)—Cl(9)	2.14(2)	Al(5)—Cl(21)	2.12(2)
Al(2)—Cl(10)	2.14(2)	Al(5)—Cl(22)	2.24(2)
Al(2)—Cl(11)	2.08(3)	Al(5)—Cl(23)	2.11(3)
Al(2)—Cl(12)	2.08(2)	Al(5)—Cl(24)	2.06(2)
Mg(3)—Cl(13)	2.48(2)	Mg(6)—Cl(25)	2.47(2)
Mg(3)—Cl(14)	2.55(3)	Mg(6)—Cl(26)	2.53(2)
Al(3)—Cl(13)	2.13(3)	Al(6)—Cl(25)	2.17(2)
Al(3)—Cl(14)	2.20(2)	Al(6)—Cl(26)	2.18(3)
Al(3)—Cl(15)	2.04(3)	Al(6)—Cl(27)	2.03(2)
Al(3)—Cl(16)	2.07(4)	Al(6)—Cl(28)	2.09(3)

* The distances are given only for the ordered ion $Al_2Cl_7^-$.

lower nuclearity of the anions, *e.g.*, $AlCl_4^-$ in complex **1** or even Cl^- in complex **5** (after extraction with methylene chloride), while a higher concentration of AlX_3 leads to the formation of anions with higher nuclearity, *e.g.*, $Al_3I_{10}^-$ in complex **8**.

In the anions $AlCl_4^-$ and $Al_2Cl_7^-$ of complex **1**, the Al atoms have a slightly distorted tetrahedral coordination with the mean Al—Cl (term.) distances 2.11 Å ($AlCl_4^-$) and 2.09 Å ($Al_2Cl_7^-$), while the Al—Cl (bridge) distances are much longer – 2.27 Å (Table 2). The $Mg[(\mu\text{-}Cl)_2AlCl_2]_3^-$ complex anion, in which a Mg atom coordinates 6 Cl atoms at a mean distance of 2.50 Å – by two Cl atoms each from the edges of three $AlCl_4^-$ tetrahedra, was first discovered in structure **4**. In this case the Al—Cl (term.) distances are 2.08 Å, and the mean Al—Cl distance in the Al—Cl—Mg bridges is 2.17 Å.

The differences in the structures of the $[\eta\text{-}C_6H_3Me_3)_3Zr_3(\mu\text{-}Cl)_6{}^{n+}$ cluster cations in complexes **1**, **2** with charge 2 and in complexes **3**, **4** with charge 3 are of special interest. Here one should take into account the rather low accuracy in determining the distances (especially the distances between light atoms) in structures **2** and **3**. In complex **2**, the factor complicating the X-ray study is the strong disordering of one of the $Al_2Cl_7^-$ anions, whereas in structure **3** there is apparently a superstructure.

Nevertheless, close values of the mean Zr—Zr distances 3.33 Å and 3.32 Å, were obtained for structures **1** and **2**, respectvely, with double-charged cations different only in the composition of the anionic part. The Zr—Zr distances in structures **3** and **4** with a triple-charged cation were much shorter – 3.27 A and 3.28 Å. The marked shortening of the distances could be caused by the fact that the HOMO in the system of molecular orbitals of the triangular cluster with charge 2, possessing 46 cluster valence electrons, is weakly antibonding.[12] When one electron is removed, the multiplicity of the Zr—Zr bonds is formally increased by 1/6, thus leading to shortening of the distances by ~0.05 Å. It should be noted that complex **6**, a hexamethylbenzene analogue of complex **2**, appears to have a somewhat longer Zr—Zr

Table 3. Bond angles (deg.) in structures **1**,**4**

Angle	ω	Angle	ω
	***Complex* 1**		
Zr(1)Cl(1)Zr(2)	81.75(9)	Zr(2)Cl(4)Zr(3)	81.8(1)
Zr(1)Cl(2)Zr(2)	81.8(1)	Zr(1)Cl(5)Zr(3)	82.2(1)
Zr(2)Cl(3)Zr(3)	82.0(1)	Zr(1)Cl(6)Zr(3)	81.7(1)
	***Complex* 4**		
Zr(1)Cl(1)Zr(1')	80.8(3)	Zr(2)Cl(3)Zr(2')	80.4(4)
Zr(1)Cl(2)Zr(1')	82.0(4)	Zr(2)Cl(4)Zr(2')	81.7(4)

distance (3.354(1) Å), probably due to the stronger donor properties of hexamethylbenzene as compared with mesitylene. At the same time, an increase in the charge of the triangular niobium cluster $[(C_6Me_6)_3Nb_3Cl_6]^{n+}$ from +1 to +2 is accompanied by only a small shortening of the Nb—Nb distance from 3.347 Å [13] to 3.333 Å,[14] probably because of the nonbonding character of the corresponding molecular orbital.

The other changes in the geometry of the cluster cation, *i.e.*, the inconsiderable decrease in the average lengths of the Zr—Cl bonds from 2.543 Å in **1** to 2.52 Å in **4** and the average angles in the Zr—Cl—Zr bridges from 81.9° in **1** to 81.2° in **4**, are mainly caused by a decrease in the Zr—Zr distances.

In light of the data obtained it appears to be necessary to test the results reported in the paper of O. E. Fischer *et al.*,[1] according to which single-charge triangular zirconium clusters (n = 1) can also exist. The fact that such complexes (with a formal oxidation degree of Zr of 2.333) were synthesized by treatment of the interaction products in the $ZrCl_4$—$AlCl_3$—Al—HMB system with water may indicate that the initially formed Zr complexes had oxidation degree 2 or even lower. As was shown in Refs. 5, 6 and confirmed by our own data, complexes of Zr(II) can arise in the reduction with aluminum. The hydrolytic disproportionation of highly charged cation complexes can be another way of forming of cluster cations.[15] The fact that further investigations, at least of trinuclear Nb clusters, confirmed the accuracy of the proposed models of the complex structure[6,13] is an indirect argument in favor of the reliability of the data given in Ref. 1. The existence of trinuclear aromatic Zr complexes with a charge from 1 to 3 would have indicated increased stability of those clusters with 45—47 cluster valent electrons, and, probably, the possibility of catalytic reactions with multielectron transfer for example, molecular nitrogen fixation, taking place in their presence.

Experimental

Synthesis of the complexes. The initial chlorides $ZrCl_4$ and $AlCl_3$ were synthesized from simple substances, purified by vacuum sublimation and kept in sealed ampules. Mesitylene (1,3,5-trimethylbenzene), which was both a reactant and a solvent, was distilled over CaH_2. The syntheses were carried out in multisection evacuated glass set-ups. The reactants were placed in the set-up in a «dry» cell filled with argon. The technique of the synthesis of complex **3**, which with minor alterations was used to produce all the other complexes, is given below.

Aluminum foil (0.20 g, 0.06 mmol), $ZrCl_4$ (4.7 g, 0.02 mmol) and $AlCl_3$ (4.0 g, 0.03 mmol) were put in one of the set-up sections; mesitylene (25—30 ml, ~0.2 mmol) was poured into another section. While cooling the section with mesitylene, the set-up was evacuated down to a pressure of ~0.05 Torr and sealed. After thawing out, mesitylene was added to a mixture of the chlorides and heated on water bath at 80—90 °C. Almost immediately the solution turned cherry-red. Some time later there appeared a dark-colored oil-like bottom layer. The duration of heating of the experiments was 3—20 h. Upon cooling to room temperature, dark-red crystals appeared in the upper, mesitylene, layer (sometimes the crystallization occurred on the Al foil surface). The liquid phases were separated by pouring them out into a vacant section. The crystals were dried in the same setup by cooling another section with liquid nitrogen, after which the sections were separated by resealing the glass neck. For the synthesis of complex **1**, a little less $AlCl_3$ (2 g, 0.015 mmol) was taken, but the reaction mixture was allowed to stand for a month after heating for 2—3 h at ~20 °C. When the molar ratio of $ZrCl_4$:$AlCl_3$ was more than 2, and the heating regime nearly the same as in preparing complex **1**, crystals of complex **2** were formed on the Al foil surface. When Zn (granules) or Mg (shavings) were used to reduce zirconium, crystalline products were also formed along with the oil-like phase. The crystal substance obtained by the reaction with Zn was analogous (by tentative conclusions) to complex **3**. The reaction with Mg upon short (2h) or long (30h) heating led to separation of one and the same phase **4**. In all the experiments the yield of the crystal substance was not high, reaching 4—6 %, and only for comlex **4** was it 8—10 %.

X-Ray study. The crystals were investigated at ~20 °C on a four-circle Enraf-Nonius CAD-4 autodiffractometer (Mo-K_α radiation, graphite monochromator, ω-scan). The crystal characteristics of complexes **1**—**4** are given in Table 1. All the crystallographical calculations were performed on a VAX computer using a package of SDP programs. In all cases the positions of the Zr atoms and partly of the Cl atoms were determined by direct methods. The coordinates of the other nonhydrogen atoms were established from difference Fourier syntheses. The positions of the H atoms were neither determined nor calculated.

For structure **1**, the least-squares refinement was made in anisotropic approximation for all the atoms. In structure **2**, one of the $Al_2Cl_7^-$ groups appeared to be disordered, at least, in two positions. The Zr atoms, the Cl atoms of the cluster ion, and the Al and Cl atoms of the ordered $Al_2Cl_7^-$ group were refined by least-squares in the anisotropic, and all the other atoms were refined in the isotropic approximation.

In structure **3**, two crystallographically independent cluster cations $[(Mes)_3Zr_3Cl_6]^{3+}$ were found. The refinement by least-squares was performed anisotropically for the Zr and Cl atoms in the cations and isotropically for all the other atoms. The comparatively high R-factor (0.12) could be associated with the presence of a superstructure (doubling of the b parameter, as was discovered through a detailed study of the crystals produced in the reduction with Zn). For structure **4**, the refinement was performed in anisotropic approxiation for the Zr and Cl atoms of the two independent cluster cations and for the Cl bridged atoms in six $Mg[(\mu\text{-}Cl)_2AlCl_2]_4^-$ anions be-

Table 4. Atomic coordinates and thermal parameters in structures **1** and **4**

Atom	x	y	z	B_{eq}/Å^2
		***Complex* 1**		
Zr(1)	0.31034(7)	0.1545(1)	0.500	3.05(2)
Zr(2)	0.29918(7)	0.39564(9)	0.53780(7)	2.90(2)
Zr(3)	0.23589(7)	0.2212(1)	0.63522(7)	2.95(2)
Cl(1)	0.4153(2)	0.2898(3)	0.5092(2)	3.47(6)
Cl(2)	0.2449(2)	0.3025(3)	0.4469(2)	4.00(7)
Cl(3)	0.3365(2)	0.3599(3)	0.6480(1)	3.38(6)
Cl(4)	0.1659(2)	0.3697(3)	0.5860(2)	3.77(7)
Cl(5)	0.3510(2)	0.1097(3)	0.6087(2)	3.88(7)
Cl(6)	0.1775(2)	0.1184(3)	0.5478(2)	4.03(7)
Cl(7)	−0.1156(3)	0.6932(4)	0.6305(3)	7.1(1)
Cl(8)	0.0727(3)	0.7938(4)	0.6488(3)	7.6(1)
Cl(9)	0.0368(3)	0.5333(4)	0.6663(4)	8.7(2)
Cl(10)	−0.0278(3)	0.6953(4)	0.7741(2)	6.3(1)
Cl(11)	−0.0885(3)	0.9369(4)	0.7425(2)	6.4(1)
Cl(12)	−0.0742(3)	0.8428(5)	0.8929(2)	6.7(1)
Cl(13)	0.0954(3)	0.8955(5)	0.8121(3)	7.5(1)
Cl(14)	0.6148(3)	0.2490(5)	0.8955(3)	8.4(2)
Cl(15)	0.4465(4)	0.2039(4)	0.9736(3)	8.9(1)
Cl(16)	0.4754(4)	0.1021(5)	0.8284(3)	9.6(2)
Cl(17)	0.4460(6)	0.3580(7)	0.8469(5)	12.8(3)
Al(1)	−0.0055(3)	0.6804(4)	0.6726(3)	5.2(1)
Al(2)	−0.0231(3)	0.8574(4)	0.8064(2)	4.4(1)
Al(3)	0.4935(3)	0.2297(4)	0.8856(3)	5.3(1)
C(1)	0.3183(9)	0.091(1)	0.3856(7)	4.5(3)
C(2)	0.2660(9)	0.029(1)	0.4195(7)	4.4(3)
C(3)	0.2960(9)	−0.032(1)	0.4683(7)	4.5(3)
C(4)	0.3762(9)	−0.019(1)	0.4859(7)	4.6(3)
C(5)	0.4226(9)	0.053(1)	0.4576(8)	4.7(4)
C(6)	0.3953(8)	0.109(1)	0.4088(7)	4.4(3)
C(7)	0.289(1)	0.143(2)	0.3293(7)	5.9(4)
C(8)	0.246(1)	−0.111(1)	0.498(1)	7.2(5)
C(9)	0.5096(8)	0.069(1)	0.4795(9)	6.0(4)
C(11)	0.2821(8)	0.582(1)	0.5717(8)	4.6(3)
C(12)	0.3651(8)	0.565(1)	0.5717(7)	4.0(3)
C(13)	0.4011(8)	0.539(1)	0.5183(7)	4.0(3)
C(14)	0.3622(8)	0.523(1)	0.4632(7)	3.8(3)
C(15)	0.2774(9)	0.547(1)	0.4616(8)	4.7(3)
C(16)	0.238(1)	0.573(1)	0.5167(7)	4.8(4)
C(17)	0.2410(9)	0.610(1)	0.632(1)	6.4(4)
C(18)	0.4930(8)	0.526(1)	0.5184(8)	4.9(4)
C(19)	0.235(1)	0.543(2)	0.4015(8)	6.7(4)
C(21)	0.1120(8)	0.177(2)	0.6947(7)	5.3(4)
C(22)	0.1373(9)	0.267(2)	0.7207(7)	6.4(4)
C(23)	0.2130(9)	0.272(1)	0.7489(7)	5.3(4)
C(24)	0.258(1)	0.187(1)	0.7487(7)	5.3(4)
C(25)	0.234(1)	0.095(1)	0.7273(7)	5.5(4)
C(26)	0.154(1)	0.090(1)	0.6962(7)	5.9(4)
C(27)	0.032(1)	0.178(3)	0.670(1)	10.9(9)
C(28)	0.240(2)	0.368(2)	0.781(1)	10.3(6)
C(29)	0.282(2)	0.001(2)	0.733(1)	10.0(6)
		***Complex* 4**		
Zr(1)	0.0118(2)	0.8980(3)	0.500	4.1(1)
Zr(2)	−0.2540(2)	0.4563(2)	0.33698(9)	3.8(1)
Cl(1)	−0.1061(7)	0.8820(7)	0.4682(2)	5.4(3)
Cl(2)	0.1196(8)	1.0119(6)	0.5305(2)	5.2(3)
Cl(3)	−0.2056(7)	0.3764(7)	0.3689(2)	5.0(3)
Cl(4)	−0.2054(7)	0.3785(7)	0.3060(2)	4.9(3)
Cl(5)	−0.2125(7)	0.3363(7)	0.4977(2)	5.9(3)
Cl(6)	−0.2052(7)	0.4382(8)	0.4435(3)	6.3(4)
Cl(7)	−0.034(1)	0.5501(9)	0.4891(3)	9.1(4)
Cl(8)	−0.0516(9)	0.368(1)	0.4522(3)	9.3(4)
Cl(9)	−0.1240(8)	0.9937(8)	0.2284(3)	7.3(4)
Cl(10)	−0.1263(9)	0.8956(9)	0.2822(3)	8.5(5)
Cl(11)	−0.280(1)	0.966(1)	0.2747(4)	10.2(5)
Cl(12)	−0.304(1)	0.788(1)	0.2389(4)	10.8(5)
Cl(13)	−0.124(1)	0.882(1)	0.3532(3)	9.5(6)
Cl(14)	−0.125(1)	0.989(1)	0.4065(3)	9.5(5)
Cl(15)	−0.293(1)	0.774(1)	0.3978(5)	15.2(7)
Cl(16)	−0.283(1)	0.942(1)	0.3602(5)	16.2(8)
Cl(17)	0.1976(7)	0.5882(8)	0.3210(2)	6.8(4)
Cl(18)	0.256(1)	0.5281(9)	0.2677(3)	8.7(5)
Cl(19)	0.119(1)	0.364(1)	0.3135(4)	11.1(5)
Cl(20)	0.037(1)	0.4676(9)	0.2740(3)	9.4(4)
Cl(21)	0.2293(8)	0.6916(7)	0.3850(2)	5.9(4)
Cl(22)	0.1971(9)	0.578(1)	0.4377(3)	9.1(5)
Cl(23)	0.039(1)	0.646(1)	0.4224(4)	13.4(7)
Cl(24)	0.044(1)	0.485(1)	0.3859(4)	12.2(6)
Cl(25)	−0.4660(9)	0.2961(9)	0.1778(3)	8.5(5)
Cl(26)	−0.445(1)	0.206(1)	0.2312(3)	12.4(7)
Cl(27)	−0.620(1)	0.074(1)	0.1919(4)	12.6(6)
Cl(28)	−0.623(1)	0.242(1)	0.2269(4)	13.3(7)
Al(1)	−0.114(1)	0.427(1)	0.4701(3)	6.5(4)
Al(2)	−0.2165(9)	0.9072(9)	0.2567(3)	5.7(4)
Al(3)	−0.215(1)	0.890(1)	0.3788(4)	8.5(5)
Al(4)	0.145(1)	0.477(1)	0.2940(4)	6.9(4)
Al(5)	0.119(1)	0.599(1)	0.4071(4)	7.7(5)
Al(6)	−0.549(1)	0.199(1)	0.2063(4)	8.3(5)
Mg(1)	−0.333	0.333	0.4723(5)	5.4(7)
Mg(2)	0.000	1.000	0.2545(5)	5.0(6)
Mg(3)	0.000	1.000	0.3785(7)	8.1(9)
Mg(4)	0.333	0.667	0.2959(5)	5.1(6)
Mg(5)	0.333	0.667	0.4119(6)	6.6(8)
Mg(6)	0.667	0.333	0.2040(7)	8.1(9)
C(1)	0.009(3)	0.767(3)	0.5243(9)	6(1)
C(2)	0.097(3)	0.816(3)	0.5133(9)	6(1)
C(3)	0.100(3)	0.823(3)	0.4885(9)	6(1)
C(4)	0.021(3)	0.782(3)	0.4736(9)	5(1)
C(5)	−0.045(4)	0.736(4)	0.484(1)	11(2)
C(6)	−0.061(3)	0.728(3)	0.5098(9)	5(1)
C(7)	0.050(4)	0.789(4)	0.554(1)	10(2)
C(8)	0.175(4)	0.848(4)	0.467(1)	10(2)
C(9)	−0.150(6)	0.676(6)	0.475(2)	15(3)
C(11)	−0.089(2)	0.585(2)	0.3356(8)	3.7(9)
C(12)	−0.134(3)	0.591(3)	0.3130(9)	5(1)
C(13)	−0.201(3)	0.614(2)	0.3164(8)	5(1)
C(14)	−0.228(2)	0.617(2)	0.3410(8)	4(1)
C(15)	−0.182(3)	0.607(3)	0.362(1)	8(2)
C(16)	−0.118(3)	0.588(3)	0.3580(9)	6(1)
C(17)	−0.006(3)	0.574(3)	0.327(1)	7(1)
C(18)	−0.247(3)	0.633(3)	0.294(1)	10(2)
C(19)	−0.209(3)	0.610(3)	0.3924(9)	6(1)

cause of the small number of reflexes. The terminal Cl, Al, Mg and C atoms were refined in isotropic approximation.

The main interatomic distances and bond angles for structures **1–4** are listed in Tables 2 and 3. Table 4 gives the atomic coordinates and thermal parameters for structures **1–4**, for which the X–ray investigation showed rather low divergence factors. The data on the interatomic distances in structures **2** and **3** are preliminary.

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