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Complexes of Alkali-Earth Metal Halides with Alkyl Aluminium Dihalides

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Abstract

Complexes of the general formula $MX_2 \cdot nRAlX_2$ have been synthesized by reaction of alkali-earth metal halides with alkyl-aluminium dihalides. Their properties, in comparison with those of analogous complexes of alkali metal halides are reported.

Introduction

It is known [1–4] that alkali metal and tetraalkylammonium halides react with $RAlX_2$ (R = alkyl, X = halide) giving stable anionic complexes of the type $M(RAlX_3)$.

Analogous complexes with alkyl aluminium compounds of weaker Lewis acidity, like R_2AlX and R_3Al, are less stable. It is, indeed, well known that the stability of these complexes depends on a critical balance of many factors such as the lattice energy of the alkali halide, the basicity of the halide anion, the energy of association and the Lewis acidity of the alkyl aluminium compound.

Complexes of alkali-earth metal halides with organo aluminium compounds are not reported; the present work was undertaken in order to verify if at least the alkylaluminium dihalides, the strongest Lewis acids among the aluminium alkyls, are able to interact with the alkali-earth metal halides.

Experimental

All the operations were carried out under dry nitrogen. Solvents were deoxygenated and carefully dried.

$(C_2H_5)_2AlCl$ and $C_2H_5AlCl_2$ were commercial products (Schering AG) distilled before use. The other alkylaluminium dihalides were prepared by proportionation of the aluminium trialkyls (Schering AG) with the appropriate amount of the related aluminium halides.

$Cl_2AlCH_2AlCl_2$ was prepared as described in [5]. Alkyl groups present in the complexes were gas volumetrically determined after decomposition with n-octyl alcohol. Gas composition was evaluated by G. L. C. Aluminium and alkali-earth metal contents were determined by atomic absorption analysis.

The analytical data of the described complexes are reported in Table I.

Synthesis of $MgCl_2 \cdot 2C_2H_5AlCl_2$ *(I)*

Anhydrous $MgCl_2$ (50.0 mmol) was added to $C_2H_5AlCl_2$ (230.0 mmol) and the mixture was heated, under stirring, at 110 °C for 5 h to obtain a solution (a shorter time is required for small particle size $MgCl_2$).

After cooling, to room temperature, n-heptane (300 ml) was added and the precipitated white powder was filtered off, washed repeatedly with n-hexane and dried *in vacuo*.

Synthesis of $CaCl_2 \cdot C_2H_5AlCl_2$ *(II)*

Anhydrous $CaCl_2$ (102.7 mmol) was added to a solution of $(C_2H_5)_3Al_2Cl_3$ (111.1 mmol) in n-heptane (100 ml) and the suspension was stirred for 60 h at room temperature. The suspended white solid was filtered off, washed repeatedly with n-hexane and dried *in vacuo*.

Synthesis of $CaCl_2 \cdot 2C_2H_5AlCl_2$ *(III)*

Anhydrous $CaCl_2$ (15.3 mmol) was added to $C_2H_5AlCl_2$ (95.0 mmol) and the mixture was heated, under stirring, at 110 °C for 5 h to obtain a solution from which, using the procedure described for complex **I**, a white powder was obtained.

Synthesis of $CaCl_2 \cdot 4C_2H_5AlCl_2$ *(IV)*

Anhydrous $CaCl_2$ (19.4 mmol) and $C_2H_5AlCl_2$ (113.4 mmol) were heated at 110 °C for 5 h under stirring. To the resulting solution, cooled to −10 °C, n-heptane (200 ml) was added and the precipitated white powder was filtered out, washed repeatedly with n-hexane and dried *in vacuo*.

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TABLE I. Analytical Data of Complexes $MX_2 \cdot nRAlX_2$[a].

	Compound	Yield (%)	Melting point[b] (°C)	Weight %			
				M	Al	X	RH[d]
(I)	$MgCl_2 \cdot 2C_2H_5AlCl_2$	77.8	135–138	6.89 (6.96)	15.61 (15.44)	61.50 (60.91)	16.00 (16.68)
(II)	$CaCl_2 \cdot C_2H_5AlCl_2$	85.8	213–315	17.00 (16.83)	11.12 (11.34)	59.53 (59.62)	11.60 (12.21)
(III)	$CaCl_2 \cdot 2C_2H_5AlCl_2$	96.7	176	11.20 (10.96)	14.65 (14.79)	58.50 (58.30)	14.85 (15.95)
(IV)	$CaCl_2 \cdot 4C_2H_5AlCl_2$	95.8	91–92	6.72 (6.49)	17.27 (17.46)	57.10 (57.26)	18.10 (18.80)
(V)	$CaBr_2 \cdot 2C_2H_5AlBr_2$	94.6	220	6.11 (6.34)	8.66 (8.53)	76.74 (75.93)	8.51 (9.20)
(VI)	$CaI_2 \cdot 2C_2H_5AlI_2$	94.8	152	4.12 (4.38)	5.87 (5.91)	84.15 (83.35)	5.72 (6.36)
(VII)	$SrCl_2 \cdot 3C_2H_5AlCl_2$	95.7	157–160	16.02 (16.25)	15.41 (15.00)	52.00 (52.60)	16.01 (16.15)
(VIII)	$BaCl_2 \cdot 3C_2H_5AlCl_2$	97.0	94	23.05 (23.61)	13.86 (13.74)	48.23 (48.15)	14.26 (14.50)
(IX)	$MgCl_2 \cdot 2CH_3AlCl_2$	80.3	163	7.30 (7.57)	16.30 (16.82)	68.00 (66.27)	8.80 (9.34)
(X)	$MgCl_2 \cdot 1.5C_4H_9AlCl_2$	72.4	237	7.62 (7.41)	13.00 (12.34)	54.83 (54.1)	23.6[c] (26.2)
(XI)	$MgCl_2 \cdot 1.5(C_8H_{17})AlCl_2$	28.2	180–185	5.90 (5.97)	10.25 (9.96)	41.70 (42.36)	40.6 (41.71)
(XII)	$MgCl_2 \cdot Cl_2AlCH_2AlCl_2$	84.8	121	7.55 (7.97)	16.90 (17.68)	64.42 (69.74)	4.50 (4.61)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] By decomposition with water. [d] GLC determination.

Synthesis of $CaBr_2 \cdot 2C_2H_5AlBr_2$ (V)

Anhydrous $CaBr_2$ (7.5 mmol), and $(C_2H_5)_3Al_2Br_3$ (40.4 mmol) were heated at 90 °C for 30 h under stirring: no solubilization was observed.

The mixture was then cooled to room temperature, suspended in n-heptane (200 ml) and a white powder recovered as described for complex **I**.

Synthesis of $CaI_2 \cdot 2C_2H_5AlI_2$ (VI)

Anhydrous $CaCl_2$ (11.7 mmol) and $(C_2H_5)_3Al_2I_3$ (50.2 mmol) were heated at 100 °C for 40 h under stirring. The resulting white complex was recovered following the procedure described for complex **V**.

Synthesis of $SrCl_2 \cdot 3C_2H_5AlCl_2$ (VII)

Anhydrous $SrCl_2$ (16.4 mmol) and $C_2H_5AlCl_2$ (113.4 mmol) were heated at 100 °C for 18 h under stirring. To the resulting solution first $(C_2H_5)_2AlCl$ (113.4 mmol) and then, after cooling to 0 °C, n-heptane (200 ml) were added. The precipitate, a white powder, was obtained as described for complex **I**.

Synthesis of $BaCl_2 \cdot 3C_2H_5AlCl_2$ (VIII)

Anhydrous $BaCl_2$ (10.3 mmol) and $C_2H_5AlCl_2$ (75.6 mmol) were heated at 50 °C for 5 h under stirring. To the resulting solution, cooled to 0 °C, $(C_2H_5)_2AlCl$ (63.7 mmol) and n-heptane (50 ml) were added and the precipitate, using the procedure described for complex **I**, was obtained as a white powder.

Synthesis of $MgCl_2 \cdot 2CH_3AlCl_2$ (IX)

Anhydrous $MgCl_2$ (14.7 mmol) and CH_3AlCl_2 (88.5 mmol) were heated at 100 °C for 5 h under stirring. To the obtained solution, cooled to 75 °C, n-heptane (150 ml) was added. The precipitated white solid was then obtained as described for complex **I**.

Synthesis of $MgCl_2 \cdot 1.5C_4H_9AlCl_2$ (X)

Anhydrous $MgCl_2$ (37.0 mmol) and $C_4H_9AlCl_2$ (150 mmol) were heated at 100 °C for 20 h under stirring. The white insoluble reaction product was then recovered as described for complex **II**.

Synthesis of $MgCl_2 \cdot 1.5C_8H_{17}AlCl_2$ (XI)

Anhydrous $MgCl_2$ (26.2 mmol) and $C_8H_{17}AlCl_2$ (219.0 mmol) were heated at 140 °C for 5 h under stirring. The mixture was filtered at this temperature; the white crystals, precipitated by cooling at 10 °C, were filtered, washed with $C_8H_{17}AlCl_2$ and then repeatedly with n-hexane, and dried *in vacuo*.

Synthesis of $MgCl_2 \cdot Cl_2AlCH_2AlCl_2$ (XII)

Anhydrous $MgCl_2$ (17.8 mmol) and $Cl_2AlCH_2AlCl_2$ (78 mmol) in CH_2Cl_2 (150 ml) were stirred under reflux for 18 h. The insoluble product was filtered off, washed repeatedly with CH_2Cl_2 at 40 °C and dried *in vacuo*.

Synthesis of $MgCl_2 \cdot 2AlCl_3$ (XIII) by Reaction of Complex I with Hydrogen Chloride

10.0 g (28.6 mmol) of complex **I** were suspended in methylene chloride (80 ml). Anhydrous hydrogen chloride, in large excess, was then bubbled through the stirred suspension at about 7 °C for 2 h. The white solid was filtered off, washed repeatedly with n-hexane and dried *in vacuo*. 9.40 g (25.9 mmol) of complex (**XIII**) were obtained. $MgCl_2 \cdot 2AlCl_3$, found, %: Mg, 6.86; Al, 15.50; Cl, 76.60; (no ethane evolved by treatment with n-octyl alcohol). Calcd., %: Mg, 6.72; Al, 14.92; Cl, 78.30.

Results and Discussion

Anhydrous MCl_2 (M = Mg, Ca) slowly dissolves in an excess of $RAlCl_2$ (R = CH_3, C_2H_5) at 110 °C; by addition at room temperature of a hydrocarbon solvent to the resulting solution, complexes **I**, **III** and **IX**, (see Table I) of general formula $MCl_2 \cdot 2RAlCl_2$ precipitate.

In spite of the insolubility of $CaBr_2$ and CaI_2 in the respective ethylaluminium dihalides, analogous complexes can be isolated (**V**, **VI**).

Complexes having different stoichiometry are obtained when the alkyl group of $RAlCl_2$ is higher than ethyl, as **X**, **XI**, or by varying the reaction conditions. Thus, for example, complex **IV**, $CaCl_2 \cdot 4EtAlCl_2$ (Et = C_2H_5), is obtained by adding, at low temperature (–10 °C), n-hexane to a solution of $CaCl_2$ in $EtAlCl_2$.

Moreover, if $CaCl_2$ reacts in hydrocarbon solution with $Et_3Al_2Cl_3$ instead of undiluted $EtAlCl_2$, the salt does not dissolve and the complex $CaCl_2 \cdot EtAlCl_2$ (**II**) can be isolated.

Strontium and barium chlorides also dissolve in $EtAlCl_2$ and complexes with the formula $Sr(Ba) \cdot AlCl_3 \cdot EtAlCl_2$ are isolated; the addition of excess Et_2AlCl before precipitation with n-heptane prevents the disproportionation of $EtAlCl_2$ and complexes $Sr(Ba)Cl_2 \cdot 3EtAlCl_2$ (**VII** and **VIII**) are obtained.

None of the investigated alkali-earth metal halides reacts either with Et_2AlCl or Et_3Al. Some attempts to prepare complexes of the type $MCl_2 \cdot nEt_2AlCl$ by reaction of $MCl_2 \cdot nEtAlCl_2$ with Et_3Al were unsuccessful owing to decomposition according to the following reaction: $MCl_2 \cdot 2EtAlCl_2 + 2Et_3Al \rightarrow MCl_2 + 4Et_2AlCl$.

All the synthesized complexes are white, microcrystalline solids which melt with decomposition. They are insoluble in hydrocarbons and only slightly soluble in chlorinated solvents; some of them dissolve in the respective alkylaluminium dihalide. Like the parent alkylaluminium dihalides, the complexes are promptly oxidized by atmospheric oxygen and react with proton active substances with evolution of the corresponding alkane. Accordingly, the reaction of $MgCl_2 \cdot 2EtAlCl_2$ with anhydrous HCl at low temperature provides a simple route to the complex $MgCl_2 \cdot 2AlCl_3$ (**XIII**).

Reaction with electron donor compounds leads to the dissociation of the complexes. For example complex **I** reacts, under mild conditions, with benzonitrile according to the following equation:

$$MgCl_2 \cdot 2EtAlCl_2 + 2C_6H_5CN \longrightarrow MgCl_2 + 2EtAlCl_2 \cdot C_6H_5CN.$$

The reported results point out remarkable analogies between the reactivity of alkali metal halides and alkali earth metal-halides toward the alkylaluminium dihalides, and between the properties of the corresponding complexes. The low stability of alkali-earth metal halide complexes, shown by their instability in the melted state, can be ascribed to the high electronegativity of these metals.

The failure to prepare complexes of the type $MCl_2 \cdot nEt_2AlCl$ is not unexpected because Et_2AlCl forms stable complexes with alkali metal halides [6] only when the electronegativity of the metal (K, Rb, Cs) is less than 0.91 [7], a value lower than the calulated one for Ba (0.97), the less electronegative alkali-earth metal.

The insolubility of the isolated complexes and the difficulty of obtaining well formed monocrystals (from $RAlX_2$ solution) prevented, up to now, the determination of their exact structure. Preliminary measurements show a valuable electrical conductivity of the solution of complex **I** in $EtAlCl_2$ [$\Lambda EtAlCl_2$ (T = 100 °C) = 1.6×10^{-6} ohm^{-1} cm^{-1}; $\Lambda MgCl \cdot 2EtAlCl_2$ in $EtAlCl_2$ (conc. = 28% by weight, T = 100 °C) = 6.5×10^{-4} ohm^{-1} cm^{-1}] thus indicating the presence of ionic species in solution.

On the basis of their properties and taking into account the analogies with the corresponding compounds of alkali metals, an essentially salt like structure could be hypothesized for this new class of complexes.

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