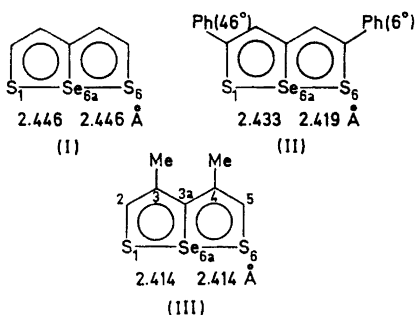selenathiophthene system. The preliminary results are given here.

The 3,4-dimethyl-6a-selenathiophthene molecule lies with the Se−C bond on a crystallographic two-fold axis, and the two halves of the molecule are therefore



exactly equal. The Se−S distances are 2.414(1) Å with the S−Se−S angle equal to 176.2(1)°. Other bond lengths in the molecule are, $S(1)-C(2) = 1.691(3)$ Å, $C(2)-C(3) = 1.375(4)$ Å, $C(3)-C(3a) = 1.420(3)$ Å, and $Se(6a)-C(3a) = 1.917(3)$ Å.

A sample of III was generously supplied by Reid.[3] The crystals are deep red and belong to the monoclinic space group $C2/c$ with the cell dimensions $a = 15.913(2)$ Å, $b = 7.503(1)$ Å, $c = 7.280(2)$ Å, and $\beta = 99.79(2)°$. There are four molecules per unit cell; $D_c = 1.824$ g/cm³, $D_m = 1.83$ g/cm³.

The structure analysis is based on X-ray data collected on a paper-tape controlled Siemens AED diffractometer using MoKα radiation. 1874 reflections were observed within $\theta = 35°$.

The structure was solved by the heavy atom method and refined by full matrix least squares. The final $R$ factor is 0.041.

We thank Dr. D. H. Reid, Department of Chemistry, The University, St. Andrews, Scotland, for a sample of 3,4-dimethyl-6a-selenathiophthene.

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Received December 13, 1972.

# The Enthalpies of Formation of the Solid Compounds K₂MgCl₄, Rb₂MgCl₄, Cs₂MgCl₄, and KMgCl₃, RbMgCl₃, CsMgCl₃

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It is well-known that compounds of the type $A_2MgCl_4$ and $AMgCl_3$ (A = K, Rb, and Cs) are found in the systems ACl-MgCl₂. For instance, the phase diagram of the system KCl-MgCl₂ has recently been examined by Grjotheim, Holm and Rotnes.[1] They found two congruently melting compounds, $K_2MgCl_4$ and $KMgCl_3$, in this system. In the case of the two systems RbCl-MgCl₂ and CsCl-MgCl₂, phase diagram examinations by Markov and Panchenko[2] show the existence of the following four congruently-melting compounds: $Rb_2MgCl_4$ and $RbMgCl_3$ in the former system, and $Cs_2MgCl_4$ and $CsMgCl_3$ in the latter. In Table 1 are given the structures and melt-
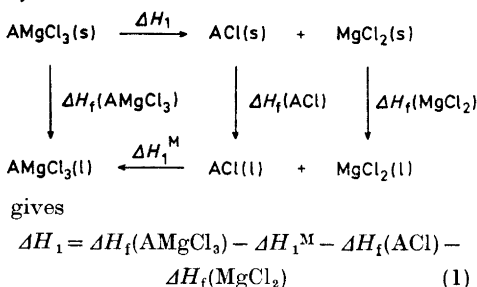
*Table 1.* Structures and melting temperatures for alkali chloride-magnesium chloride compounds.

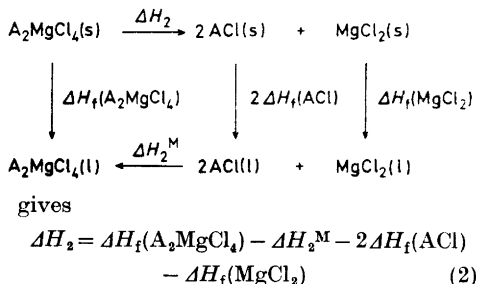| Compound | Structure [3] | $T_f$/K |
|---|---|---|
| K₂MgCl₄ | tetragonal | 705[1] |
| Rb₂MgCl₄ | tetragonal | 740[2] |
| Cs₂MgCl₄ | orthorhombic | 813[2] |
| KMgCl₃ | hexagonal | 755[1] |
| RbMgCl₃ | hexagonal | 825[2] |
| CsMgCl₃ | hexagonal | 883[2] |

ing points of the six compounds. The structures have been determined by Svedahl.[3]

While the enthalpies of mixing in the liquid state have been determined,[4] the enthalpies of reaction between the solid compounds are not known. These enthalpies can, however, be calculated from enthalpy data as shown by the following two cycles.

Cycle I:

AMgCl$_3$(s) $\xrightarrow{\Delta H_1}$ ACl(s)  +  MgCl$_2$(s)

$\downarrow \Delta H_f$(AMgCl$_3$)    $\downarrow \Delta H_f$(ACl)    $\downarrow \Delta H_f$(MgCl$_2$)

AMgCl$_3$(l) $\xleftarrow{\Delta H_1{}^M}$ ACl(l)  +  MgCl$_2$(l)

gives

$$\Delta H_1 = \Delta H_f(\text{AMgCl}_3) - \Delta H_1{}^M - \Delta H_f(\text{ACl}) - \Delta H_f(\text{MgCl}_2) \qquad (1)$$

Cycle II:

A$_2$MgCl$_4$(s) $\xrightarrow{\Delta H_2}$ 2 ACl(s)  +  MgCl$_2$(s)

$\downarrow \Delta H_f$(A$_2$MgCl$_4$)    $\downarrow 2\Delta H_f$(ACl)    $\downarrow \Delta H_f$(MgCl$_2$)

A$_2$MgCl$_4$(l) $\xleftarrow{\Delta H_2{}^M}$ 2 ACl(l)  +  MgCl$_2$(l)

gives

$$\Delta H_2 = \Delta H_f(\text{A}_2\text{MgCl}_4) - \Delta H_2{}^M - 2\Delta H_f(\text{ACl}) - \Delta H_f(\text{MgCl}_2) \qquad (2)$$

In the following the enthalpies $\Delta H_1$ and $\Delta H_2$ are calculated at 700 K, a temperature which is below the melting points of all six compounds.

The enthalpies of fusion and of mixing used in the calculation are summarized in Tables 2 and 3. The enthalpies of mixing for the compounds were measured by Kleppa and McCarty[4] at 1073 K and 993

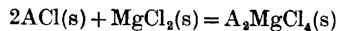*Table 2.* Enthalpies of fusion at 700 K used in the calculations.

| Compound | $\Delta H_f$ | Ref. |
|---|---|---|
| | kcal mol$^{-1}$ | |
| KCl | 6.0 | 6, 7 |
| RbCl | 5.4 | 6, 7 |
| CsCl | 4.6 | 6, 7 |
| MgCl$_2$ | 9.1 | 8 |
| KMgCl$_3$ | 10.1 | 5 |
| RbMgCl$_3$ | 12.1 | 5 |
| CsMgCl$_3$ | 13.5 | 5 |
| K$_2$MgCl$_4$ | 10.7 | 5 |
| Rb$_2$MgCl$_4$ | 11.9 | 5 |
| Cs$_2$MgCl$_4$ | 8.8 | 5 |

*Table 3.* Enthalpies of mixing of 2ACl(l)+ MgCl$_2$(l) = A$_2$MgCl$_4$(l) ($\Delta H_2{}^M$) and ACl(l)+ MgCl$_2$(l) = AMgCl$_3$(l) ($\Delta H_1{}^M$) at 700 K.
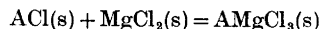
| Mixing process | $\Delta H^M$ | Ref. |
|---|---|---|
| | kcal mol$^{-1}$ | |
| 2KCl + MgCl$_2$ | − 16.2 | 4, 5 |
| 2RbCl + MgCl$_2$ | − 17.7 | » |
| 2CsCl + MgCl$_2$ | − 19.5 | » |
| KCl + MgCl$_2$ | − 8.4 | » |
| RbCl + MgCl$_2$ | − 9.2 | » |
| CsCl + MgCl$_2$ | − 10.2 | » |

K. The values at 700 K have been calculated by use of their data and the heat capacities given by Holm *et al.*[5] The enthalpies of fusion of the alkali chlorides are those given by Dworkin and Bredig.[6]

The enthalpies of formation from the simple chlorides

$$2\text{ACl(s)} + \text{MgCl}_2\text{(s)} = \text{A}_2\text{MgCl}_4\text{(s)}$$

and

$$\text{ACl(s)} + \text{MgCl}_2\text{(s)} = \text{AMgCl}_3\text{(s)}$$

have been calculated directly from the cycles at 700 K and the enthalpies transferred to 298.15 K by use of enthalpy increment data for KCl, RbCl, and CsCl given in JANAF[9] and for the complex compounds given by Holm *et al.*[5] The

*Table 4.* Enthalpies of reaction of ACl(s)+ MgCl$_2$(s) = AMgCl$_3$(s) and 2ACl(s)+ MgCl$_2$(s) = A$_2$MgCl$_4$(s) at 298.15 K and 700 K (estimated uncertainties ± 1 kcal).

| Compound | $\Delta H$/kcal mol$^{-1}$ | |
|---|---|---|
| | 700 K | 298.15 K |
| KMgCl$_3$ | − 3.4 | − 3.7 |
| RbMgCl$_3$ | − 6.8 | − 6.8 |
| CsMgCl$_3$ | − 10.0 | − 10.0 |
| K$_2$MgCl$_4$ | − 5.5 | − 8.5 |
| Rb$_2$MgCl$_4$ | − 9.7 | − 12.3 |
| Cs$_2$MgCl$_4$ | − 10.0 | − 12.0 |

results are given in Table 4. In Table 5 are given the enthalpies of the reactions

$$2\text{AMgCl}_3\text{(s)} = \text{A}_2\text{MgCl}_4\text{(s)} + \text{MgCl}_2\text{(s)}$$

for A = K, Rb, and Cs. As can be seen from this table the stability of AMgCl$_3$ increases

*Table 5.* Enthalpies of disproportionation $2AMgCl_3(s) = A_2MgCl_4(s) + MgCl_2(s)$, (estimated uncertainties $\pm 1$ kcal).

| Reaction | $\Delta H_{700}$ kcal mol$^{-1}$ | $\Delta H_{298.15}$ kcal mol$^{-1}$ |
|---|---|---|
| $2KMgCl_3(s) = $ $K_2MgCl_4(s) +$ $MgCl_2(s)$ | $+1.3$ | $-1.1$ |
| $2RbMgCl_3(s) =$ $Rb_2MgCl_4(s) +$ $MgCl_2(s)$ | $+3.9$ | $+1.3$ |
| $2CsMgCl_3(s) =$ $Cs_2MgCl_4(s) +$ $MgCl_2(s)$ | $+10.0$ | $+8.0$ |

considerably from the potassium to the cesium compound.

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# Calculation of C=C and C—F Bond Lengths in $CH_2=CH_2$, $CH_2=CHF$, *cis*-$CHF=CHF$, and $CH_2=CF_2$

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Experimental observations of $C=C$ and $C-F$ bond lengths in ethylene and fluorinated ethylenes (Table 1) indicate decreasing lengths with progressing fluorination. Earlier "resonance" structures such as $\overline{C}H_2 - CH = \overset{+}{F}$ would seem to connect increasing $C=C$ length with decreasing $C-F$ length. This communication reports results of *ab initio* calculations of the molecules of Table 1 in which the molecular energy was separately minimized with respect to the $C=C$ and $C-F$ bond(s) in that order, taking remaining geometrical parameters from Refs. 1 – 3. A relatively small, Gaussian basis set[4] $(s,p=7,3$ contracted to 4,2) was used. The set was tested to see how well the experimental carbon-carbon distances in ethane $(r_z = 1.532$ Å),[5] in ethylene $(r_z = 1.335$ Å),[1] and in acetylene $(r_e = 1.203$ Å)[6] were reproduced. The results $(r_e)$ were 1.554, 1.314, and 1.188 Å, respectively. Obviously, to assign significance to what follows one must assume that somehow the molecules of Table 1 are more "related" than $C_2H_6$, $C_2H_4$, and $C_2H_2$.

The results of Table 2 are a minor part of a more comprehensive investigation.[7] To the best of our knowledge only one paper[8] based on the experimental structure of $CH_2 = CHF$ (Table 1) has appeared earlier. At the present level of approximation the calculated bond lengths of Table 2 show the same trends as the experiments. The computed gross atomic charges show that carbon in ethylene, when binding fluorine instead of hydrogen, donates *ca.* 0.6 e $(\sim 6.3965$ (col. 1) $- 5.7818$ (col.2) $\sim 6.3965 - 5.8433$ (col.3) $\sim 0.5(6.3965 - 5.2163)$ (col.4)) to fluorine, the hydrogen gross electronic charges (not quoted) being practically constant (0.8 e). Unsubstituted C prac-

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