# Complexes between Gaseous Gallium Chloride and Cobalt Chloride

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In gaseous gallium chloride, Co^{2+} is found as $CoGa_2Cl_8$ with the following thermodynamic functions of formation at 673 K:

$$CoCl_2(s) + Ga_2Cl_6(g) = CoGa_2Cl_8(g)$$
$$\Delta H^\circ = 43.9 \pm 0.7 \text{ kJ}, \quad \Delta S^\circ = 36.9 \pm 1.1 \text{ J K}^{-1}$$
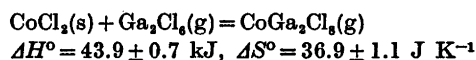
The structure of $CoGa_2Cl_8$ is discussed, and a coordination of $CoCl_2$ to the Ga_2Cl_6 molecule, without breaking the double bond in Ga_2Cl_6, is suggested. An octahedral coordination of Co^{2+} is considered unlikely.

As an extension of a general study of gas complexes between $AlCl_3$ and divalent $3d$-metal chlorides [1-3] it was decided to investigate the complexing properties of $GaCl_3$ with respect to $CoCl_2$.

Gaseous $GaCl_3$ and $AlCl_3$ have very similar structural and thermodynamic properties, both being subject to the equilibrium

$$A_2Cl_6(g) = 2ACl_3(g), \quad A = Al, \ Ga \qquad (1)$$
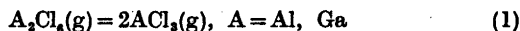
which is shifted to the right with increasing temperature. However, in spite of their similarities it is of interest to determine how the heavier Ga^{3+} ion compares to Al^{3+} for the general complexing reaction:

$$MCl_2(s,g) + n_2A_2Cl_6(g) = MA_{2n_2}Cl_{6n_2+2}(g) \qquad (2)$$
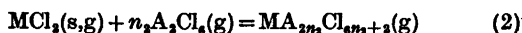
with $CoCl_2$ as the metal chloride in the present study. Although $GaCl_3$ is more difficult to handle than $AlCl_3$, the experiments were expected to benefit from the shift to the left of the side reaction:

$$2A_2Cl_6(g) + 3SiO_2(s) = 2A_2O_3(s) + 3SiCl_4(g) \qquad (3)$$

when substituting Ga_2Cl_6 for Al_2Cl_6.

The chosen experimental method was absorption spectroscopic determination of the pressure of the gas complex in closed quartz cells according to eqn. (2). This method has been described in detail previously.[1,4]

The molar absorption of a known amount of MCl_2 in the gas phase is first determined by the equation:

$$\varepsilon^i_{Co-Ga-Cl} = A^i V/nl \qquad (4)$$

whereafter the pressure of the gas complex in the presence of $MCl_2(s)$ is determined by

$$P_{Co-Ga-Cl} = \frac{A^i R \overline{T}}{\varepsilon^i_{Co-Ga-Cl} l} \qquad (5)$$

$\varepsilon^i_{Co-Ga-Cl}$: molar absorptivity of the gas complex at wavelength i, A: optical density at wavelength i, V: volume, n: mol of gas complex, l: optical path length, P: pressure of gas complex, R: gas constant and $\overline{T}$: mean cell temperature.

The pressure of Ga_2Cl_6 as well as the temperature were varied so that the stoichiometry and the thermodynamic functions for the reaction corresponding to eqn. (2) could be obtained.

EXPERIMENTAL

Anhydrous $GaCl_3$ was obtained in ampoules as 99.99 % (Schuchardt, München, DBR) and no further purification was performed. Anhydrous $CoCl_2$ was prepared from $CoCl_2.6H_2O$ "pure" (Koch-Light Labs., Colubrook, England) by heating under vacuum at 120 °C for 4 h,

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followed by purging with HCl for 2 h at 450 °C, and then repeated sublimation.

The experimental procedure has been described previously.[1,5] Equilibrium was found to be established within 30 min, at which time the spectrum was recorded.

RESULTS

Spectrophotometrically the gas complex formation between $CoCl_2(s)$ and $GaCl_3$ was detected above 280 °C by the appearance of two composite absorption bands at about 15.6 and 7.1 kK (Fig. 1). By analyzing the spectrum in detail, absorption maxima and shoulders were observed at the following wave numbers [expressed in kK with the molar absorptivities at 400 °C given in parenthesis (Exp. 2, Table 1)]: 14.9(85), 15.6(150), 16.8(140), 17.6(sh), 18.5(sh), 7.1(30), 5.9(−).

Due to the composite nature of the two main absorption regions, individual spectral half-widths could not be given, but would probably not exceed 2 kK.

The molar absorptivity for the strongest peak was determined in three experiments specified in Table 1. The molar absorptivity decreased with increasing temperature and did not reveal any dependence on the pressure of Ga_2Cl_6 above 400 °C. Between 300 and 400 °C a small decrease in molar absorptivity with increasing Ga_2Cl_6 pressure may be present, similar to what is observed by Dell'Anna and Emmenegger [6] for the $CoCl_2 - Al_2Cl_6$ gas complex. Statistically, however, the pressure dependence was not significant on a 90 % confidence level, and all the molar absorptivity
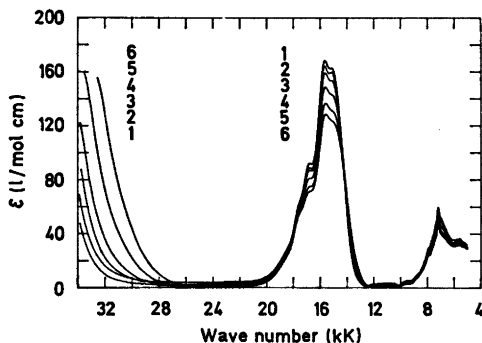

Fig. 1. Absorption spectra of $CoCl_2$ in gaseous Ga_2Cl_6 (Exp. 2). Temperatures are given in K. Curves 1, 575; 2, 625.5; 3, 678; 4, 726.5; 5, 782; 6, 821.

data were fitted to the following pressure-independent equation with a 2.5 % standard deviation:

$$\varepsilon^{15.6}_{\text{Co-Ga-Cl}} =$$
$$-36.4 + 0.685\overline{T} - 6.017 \times 10^{-4}\overline{T^2} \qquad (6)$$

Eqn. (6) was used for determining the vapour pressure of the complex in the experiments with excess $CoCl_2$ (Table 1, Exp. 4 − 9).

Using a non-linear regression analysis program by Hertzberg,[7] previously described by Øye and Gruen,[4] the experiments were best described by the following complexing equilibrium:

$$CoCl_2(s) + Ga_2Cl_6(g) = CoGa_2Cl_8(g)* \qquad (7)$$
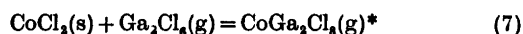
$$P_{\text{CoGa}_2\text{Cl}_8} = P_{\text{Ga}_2\text{Cl}_6} \exp_{10}\left(1.936 - \frac{2295}{T_{\min}}\right) \qquad (8)$$

corresponding to $\Delta H° = 43.9 \pm 0.7$ kJ and $\Delta S° = 36.9 \pm 1.1$ J K^{-1} at 673 K. The standard deviation in the estimate was 9.5 %. The pressure of the dimer, $P_{\text{Ga}_2\text{Cl}_6}$, was calculated by the ideal-gas law using the weighed-in amount of $GaCl_3$ and correcting for the amount consumed in the complexing and dissociation reaction:[8]

$$Ga_2Cl_6(g) = 2GaCl_3(g),$$
$$\log_{10}K(\text{atm}) = -4595/T + 7.066 \qquad (9)$$

DISCUSSION

The expected absence of the side reaction due to attack of the quartz cuvette [eqn. (3)] by using $GaCl_3$ instead of $AlCl_3$ was experimentally verified. A loaded cell was left at 425 °C for 5 days without any detectable spectral changes. Even with this excellent stability and good reproducibility shown by repeated experiments, the fit to the model equations was not any better than the results with $AlCl_3$.[1] The reason may be that some $GaCl_3$ after all did evaporate at the filling of the cell.

Assuming constant temperature and a one-species model, the stoichiometric constant according to eqn. (2) may be calculated by using

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* The method does not unambigously exclude the presence of polynuclear Co-species as $Co_2Ga_2Cl_{10}$,[4] but they are considered unlikely.

Table 1. Co—Ga—Cl gas complexes. Molar absorptivity at 15.6 kK (Exp. 1—3) and calculated vapour pressure in presence of $CoCl_2(s)$ (Exp. 4—9).

Exp. No.	Specification	T_{min} (K)	$\overline{T}$ (K)	Optical density A	Molar absorptivity $\varepsilon_{Co-Ga-Cl}$ (l/mol cm)	$P_{Co-Ga-Cl}$ (atm)
1	$P^\circ_{Ga_2Cl_6}=1.276\times10^{-3}\overline{T}$	671	677	0.275	158.8	
	$l=14.2$ cm	721.5	728.5	0.255	147.2	
	$V=76.73$ cm^3	770	778	0.230	132.8	
	$w_{CoCl_2}=1.215$ mg	808	817	0.210	121.3	
2	$P^\circ_{Ga_2Cl_6}=3.417\times10^{-3}\overline{T}$	571	575	0.560	162.3	
		620.5	625.5	0.555	160.9	
	$l=14.2$ cm	672	678	0.520	150.7	
	$V=76.73$ cm^3	719.5	726.5	0.490	142.0	
	$w_{CoCl_2}=2.42$ mg	774	782	0.445	129.0	
		812	821	0.420	121.8	
3	$P^\circ_{Ga_2Cl_6}=7.34\times10^{-3}\overline{T}$	570	571	0.520	153.6	
		600	601	0.530	156.5	
	$l=5.0$ cm	653	654	0.510	150.6	
	$V=14.22$ cm^3	708	709	0.480	141.7	
	$w_{CoCl_2}=1.26$ mg	762	763	0.450	132.9	
		817.5	818.5	0.415	122.6	
4	$P^\circ_{Ga_2Cl_6}=0.303\times10^{-3}\overline{T}$	492.5	495.5	0.017	155.3	2.97×10^{-4}
		540.5	544.5	0.032	158.2	6.03×10^{-4}
	$l=15.0$ cm	588.5	593.5	0.051	158.2	10.50×10^{-4}
	$V=58.04$ cm^3	640.5	646.5	0.063	155.0	14.30×10^{-4}
		692	699	0.059	148.4	15.20×10^{-4}
		743	751	0.047	138.7	13.90×10^{-4}
		796	805	0.0355	125.1	12.50×10^{-4}
5	$P^\circ_{Ga_2Cl_6}=0.71\times10^{-3}\overline{T}$	522	525	0.065	157.4	1.19×10^{-3}
		574.5	578.5	0.125	158.5	2.50×10^{-3}
	$l=15.0$ cm	632.5	637.5	0.200	155.8	4.48×10^{-3}
	$V=55.86$ cm^3	693.5	699.5	0.230	148.3	5.93×10^{-3}
		738	745	0.215	140.0	6.26×10^{-3}
		790	798	0.180	127.1	6.18×10^{-3}
6	$P^\circ_{Ga_2Cl_6}=1.455\times10^{-3}\overline{T}$	535	538	0.180	155.0	3.40×10^{-3}
		583	587	0.325	158.4	6.55×10^{-3}
	$l=15.1$ cm	628	633	0.495	156.1	10.91×10^{-3}
	$V=44.06$ cm^3	677	683	0.630	150.8	15.51×10^{-3}
		726	733	0.675	142.4	18.88×10^{-3}
		774.5	782.5	0.645	131.2	20.91×10^{-3}
		817	826	0.580	118.9	21.90×10^{-3}
7	$P^\circ_{Ga_2Cl_6}=1.50\times10^{-3}\overline{T}$	585	586	0.115	158.4	6.98×10^{-3}
		643.5	644.5	0.190	155.1	12.96×10^{-3}
	$l=5.0$ cm	700	701	0.250	148.1	19.42×10^{-3}
	$V=15.12$ cm^3	756	757	0.235	137.3	21.26×10^{-3}
		810.5	811.5	0.210	123.2	22.70×10^{-3}
8	$P^\circ_{Ga_2Cl_6}=2.94\times10^{-3}\overline{T}$	541	542	0.160	158.1	9.00×10^{-3}
		591.5	592.5	0.290	158.2	17.83×10^{-3}
	$l=5.0$ cm	646	647	0.470	154.9	32.22×10^{-3}
	$V=14.84$ cm^3	699	700	0.625	148.3	48.42×10^{-3}
		706	707	0.620	147.1	48.91×10^{-3}
		752	753	0.700	138.2	62.60×10^{-3}
		808	809	0.690	124.0	73.88×10^{-3}
9	$P^\circ_{Ga_2Cl_6}=7.42\times10^{-3}\overline{T}$	564	568	$(2.27)^a$	158.6	(4.45×10^{-2})
		604.5	609	(3.10)	157.6	(6.55×10^{-2})
	$l=15.0$ cm	643.5	649	(4.05)	154.7	(9.29×10^{-2})
	$V=5$ cm^3	672	678	(4.50)	151.4	(11.02×10^{-2})

^{a} Uncertain values.

the experiments with excess $CoCl_2$ at different Ga_2Cl_6 pressures. Referred to exp. 8 (Table 1), typical values between 0.96 and 1.08 are obtained at 394 °C, while slightly higher values were found at the lowest temperatures. In spite of these deviations from the value $n_2 = 1$, corresponding to $CoGa_2Cl_8(g)$, a two-species model [e.g. $CoGa_2Cl_8(g) - CoGa_3Cl_{11}(g)$ or $CoGa_2Cl_8(g) - CoGa_4Cl_{14}(g)$] did not improve the standard deviation relative to a one-species model with $CoGa_2Cl_8(g)$ present. In conclusion, $CoGa_2Cl_8(g)$ is considered to be the main gas species, but small amounts of $CoGaCl_5(g)$, $CoGa_3Cl_{11}(g)$ or $CoGa_4Cl_{14}(g)$ may be present.

Referring to Table 1, Exp. 4 and 5, it may seem curious that $P_{CoGa_2Cl_8}$ is decreasing with increasing temperature for the very highest temperatures in spite of a positive ΔH of the reaction given by eqn. (7). This is, however, consistent with the present model given by eqns. (7) and (8) and is simply due to dissociation of Ga_2Cl_6 [eqn. (9)].

The spectral data do not lend themselves to any unambiguous conclusion as to the geometric arrangement of chloride around the cobalt. The molar absorptivity is between the values one might expect for the octahedral and tetrahedral geometries, however, closer to those of octahedral geometry. The variation with temperature, however, is similar to that for a tetrahedral species,[9,10] and thus the octa-

hedral coordination of Co^{2+} is considered highly unlikely. However, the possibilities of other geometries cannot be excluded.

The present experimental results for $CoCl_2 - GaCl_3$ are parallel to some very recent results on $CoCl_2 - AlCl_3$ gas complexes by Dell'Anna and Emmenegger,[6] Papatheodorou,[11] Thistlethwaite and Ciach,[12] as well as a previous study by Dewing.[13] They all find the main gas complex to be $CoAl_2Cl_8$ (as compared to $CoGa_2Cl_8$), and the spectral results are all very similar for the Al as well as the Ga containing complex. The main peak is found around 16 kK with a decrease in molar absorptivity with increasing temperature.
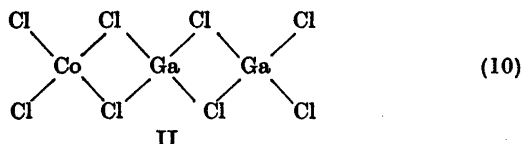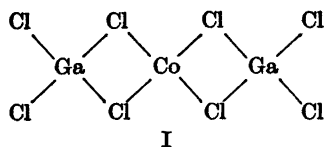
Table 2 gives the thermodynamic functions for gas complexation of $CoCl_2(s)$ as well as the dissociation of $Al_2Cl_6(g)$ and $Ga_2Cl_6(g)$. The entropy of dissociation of $Al_2Cl_6(g)$ and $Ga_2Cl_6(g)$ is seen to be the same. The entropy of complexation of $CoCl_2(s)$ with either $Al_2Cl_6(g)$ or $Ga_2Cl_6(g)$ is also seen to be equal, confirming the assumption of a similar structure of the two gas complexes. The remarkable feature of Table 2, however, is that the enthalpy of complexation is equal for the Al and the Ga containing complexes, in spite of the fact that the enthalpies of dissociation of $Al_2Cl_6(g)$ and Ga_2Cl_6 differ by 30 kJ. This suggests that the Al_2Cl_6 and Ga_2Cl_6 molecules remain essentially intact and do not dissociate, the $CoCl_2$ co-

Table 2. Thermodynamic functions for gas complex formation and dissociation reactions.

Ref.	Temp. K	$\Delta H°$ kJ	$\Delta S°$ J K^{-1}	K atm.
$Al_2Cl_6(g) = 2AlCl_3(g)$				
14	673	118	135	0.008
$Ga_2Cl_6(g) = 2GaCl_3(g)$				
8	673	88	135	1.7
$CoCl_2(s) + Al_2Cl_6(g) = CoAl_2Cl_8(g)$				
13	750	53.5	51.9	11.4×10^{-2}
6[a]	673	43.1 ± 2.2	39.3 ± 2.8	5.1×10^{-2}
11	673	41.8 ± 0.8	41.0 ± 1.3	7.9×10^{-2}
12	673	42.0 ± 0.7	45.0	12.3×10^{-2}
$CoCl_2(s) + Ga_2Cl_6(g) = CoGa_2Cl_8(g)$				
This work	673	43.9 ± 0.7	36.9 ± 1.1	3.3×10^{-2}

[a] Mean value of three methods.

ordinating at the end of the molecule, for instance approximately tetrahedrally in fashion II rather than I:

$$
\begin{array}{cccccccc}
Cl & & Cl & & Cl & & Cl \\
\diagdown & \diagup & & \diagdown & \diagup & & \diagdown & \diagup \\
 & Ga & & Co & & Ga & \\
\diagup & & \diagdown & & \diagup & & \diagdown \\
Cl & & Cl & & Cl & & Cl
\end{array}
$$

$$\text{I}$$

$$
\begin{array}{cccccccc}
Cl & & Cl & & Cl & & Cl \\
\diagdown & \diagup & & \diagdown & \diagup & & \diagdown & \diagup \\
 & Co & & Ga & & Ga & \\
\diagup & & \diagdown & & \diagup & & \diagdown \\
Cl & & Cl & & Cl & & Cl
\end{array}
\qquad (10)
$$

$$\text{II}$$

Dell'Anna and Emmenegger [6] describe the Co coordination in $CoAl_2Cl_8$ as tetrahedral, whereas Papatheodorou [11] and Thistlethwaite and Ciach [12] describe it as mainly octahedral. Papatheodorou [11] explains the increase of molar absorptivity with decreasing temperature as due to small amounts of tetrahedrally coordinated Co^{2+} in equilibrium with the octahedral form, the tetrahedral coordination being more prevalent at lower temperatures.

We are at variance with this interpretation because it infers that the equilibrium

$$Co(tetr)Al_2Cl_8(g) = Co(oct)Al_2Cl_8(g) \qquad (11)$$

has $\Delta H > 0$ and, since $K > 1$, $\Delta S > 0$. The signs of the thermodynamic functions are both opposite to what is expected. Whether structure I or II is assumed for a tetrahedral structure, a tetrahedral-octahedral transformation will result in the formation of two additional $Co - Cl$ bonds with an expected negative ΔH. The vibrational entropy cannot be anticipated to counteract the negative rotational entropy [11] for eqn. (11). The main contribution to the vibrational entropy is given by the low frequency torsional vibrations and they are expected to be lower for the more loosely bonded $AlCl_4^-$ in the tetrahedral coordination, hence resulting in $\Delta S < 0$ for eqn. (11) both due to rotational and vibrational entropy.

It should, however, be stressed that the coordination equilibria in liquid and gaseous aluminium chloride still are intriguing. Co^{2+} and Ti^{2+} both have a similarly low octahedral site stabilization energy, but Ti^{2+} coordinates octahedrally in both the liquid and gaseous alu-

minium chloride,[2] while octahedral coordination of Co^{2+} is only found in liquid aluminium chloride.[10]

From a practical point of view it should be mentioned in conclusion that in spite of the similar thermodynamic properties of gas complex formation, Ga_2Cl_6 becomes less effective at higher temperatures due to its ease of dissociation relative to Al_2Cl_6. The greater stability of Ga_2Cl_6 in the presence of SiO_2 may, however, make it more attractive for detailed optical studies.

REFERENCES

1. Anundskås, A. and Øye, H. A. *Inorg. Nucl. Chem. 37* (1975) 1609.
2. Sørlie, M. and Øye, H. A. To be published.
3. Sutakshuto, S. and Øye, H. A. To be published.
4. Øye, H. A. and Gruen, D. M. *J. Am. Chem. Soc. 91* (1969) 2229.
5. Anundskås, A., Mahgoub, A. E. and Øye, H. A. *Egypt. J. Chem. In print.*
6. Dell'Anna, A. and Emmenegger, T. P. *Helv. Chim. Acta 58* (1975) 1145.
7. Hertzberg, T. "MODTLP" Report. Inst. for kjemiteknikk, Norges tekniske høgskole, Trondheim 1970.
8. Fischer, W. and Jübermann, O. *Z. Anorg. Allgem. Chem. 227* (1936) 227.
9. Gruen, D. M. and McBeth, R. L. *Pure Appl. Chem. 6* (1963) 23.
10. Øye, H. A. and Gruen, D. M. *Inorg. Chem. 4* (1965) 1173.
11. Papatheodorou, G. N. *Z. Anorg. Allgem. Chem. 411* (1975) 153.
12. Thistlethwaite, P. J. and Ciach, S. *Inorg. Chem. 14* (1975) 1430.
13. Dewing, E. W. *Metall. Trans. 1* (1970) 2169.
14. *JANAF Thermochemical Tables*, (Directors Stull, D. R. and Prophet, H.) Nat. Stand. Ref. Data Sci., Nat. Bur. Stand. 37, Washington 1971.

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