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Vaporization of Neodymium Chloride as a Gaseous Complex of Gallium Trichloride

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The formation of gaseous complexes between $NdCl_3$ and $GaCl_3$ has been studied by absorption spectroscopy in the temperature range 600–1000 K and at total pressures ranging from 5 to 20 atm. Thermodynamic model calculations indicate a stepwise buildup of the gas complexes with formation of the molecules $NdGaCl_6$, $NdGa_2Cl_9$, $NdGa_3Cl_{12}$, and $NdGa_4Cl_{15}$.

Introduction

The formation of gas complexes between metal halides and group 3 metal halides has received considerable attention in recent years; see ref 1–4 for reviews.

The system $NdCl_3$–$AlCl_3$ has been studied by Øye and Gruen,[5] and the gas complexes $NdAl_3Cl_{12}$ and $NdAl_4Cl_{15}$ were found. Samples contained in sealed quartz cuvettes were studied by absorption spectroscopy. Due to a reaction between $AlCl_3$ and SiO_2 above 500 °C, the equilibria could not be investigated over an extended temperature interval. Even below 500 °C the equilibrium time was limited by a slight reaction. As $GaCl_3$ does not react with SiO_2, the successive gas complex formation in the $NdCl_3$–$GaCl_3$ system can be investigated over an extended temperature and time span. Monomeric and dimeric $GaCl_3$ complexes do not absorb light in the visible spectral range. The vapor pressure and molar absorption coefficient of uncomplexed $NdCl_3(g)$ are so small[6,7] that the spectrum is due solely to $NdCl_3$–$GaCl_3$ gas complexes.

The principle of high-temperature gas complex formation investigated by the absorption spectroscopic method is described by Øye and Gruen,[5] and only a brief summary is given here. The system under study, $NdCl_3$–$GaCl_3$, is contained in closed optical cells. When the sample is heated, $NdCl_3$–$GaCl_3$ species are formed in the vapor phase. In order to determine the partial pressure of the complex species, the molar absorption coefficient of the complexed Nd^{3+} ion at a specific wavenumber has to be established. This is done by measuring the optical density in experiments where a small amount of $NdCl_3$ in the cell is completely evaporated as a gas complex. At a certain wavenumber ν_j the molar absorption coefficient of the complex can be calculated from Beer's law

$$\epsilon_c(\nu_j) = \frac{[A(\nu_j)]V}{nl} \tag{1}$$

when it is assumed that the amount of uncomplexed $NdCl_3(g)$ is negligible.

When the molar absorption coefficient of the complex at ν_j is known, the partial pressure of the complex species can be determined in experiments where the vapor is in equilibrium with a condensed phase:

$$P_c = \frac{[A(\nu_j)]R\bar{T}}{[\epsilon_c(\bar{\nu}_j)]l} \tag{2}$$

Equation 2 is derived from eq 1 by introducing the ideal gas law and solving for P_c. In eq 1 and 2 P_c = partial pressure of gaseous complex (atm) (1 atm = 1.01325 × 10^5 Pa), $A(\nu_j)$ = measured optical density at wavenumber ν_j, R = gas constant (L·atm/(mol·K)), $\bar{T}$ = average cell temperature (K), l = optical path length (cm), V = volume of the cell (L), and n = number of moles of gas complex.

If more than one gas complex is present, the complex formation reaction can be formulated

$$n_i NdCl_3(s,l) + m_i Ga_2Cl_6(g) = Nd_{n_i}Ga_{2m_i}Cl_{6m_i+3n_i}(g) \tag{3}$$

when n_i and $2m_i$ are integers. In this case eq 2 is expressed as

$$P_c = \sum_i n_i[P(Nd_{n_i}Ga_{2m_i}Cl_{6m_i+3n_i})] \tag{4}$$

Experimental Section

Apparatus. Commercially available optical quartz cells (Hellma GmbH & Co., Müllheim/Baden, West Germany) were used. The cells had optical path lengths of 20.00 cm, inner diameters of 15 mm, and 2-mm wall thickness. Prior to use, all cells were annealed in a furnace by rapidly increasing the temperature to 1150 °C and cooling slowly to less than 200 °C over a 24-h period. This was done to avoid cracking of the cells during the experiments. The cell volumes were determined by pycnometric weighing.

The furnace has previously been described by Anundskås and Øye.[8] It is horizontal and cylindrical and has five Kanthal wound heating elements along the tube. Each element was differentially regulated with respect to the middle zone by separate Eurotherm PID controllers (Eurotherm Ltd., Sussex, England). By adjusting the set point of the controller, the desired temperature profile along the tube could be achieved. The temperature in the middle zone was kept lower than in the end zones in order to prevent condensation of the vapor on the cell windows. The temperature profile through the furnace was measured at different controller settings along the axis of a dummy cell with the same optical path length as that of the actual cells. The temperature during an experiment was measured near the middle of the cell, close to the outside cell wall.

A rigid stainless steel cell holder with radiation shields was used to keep the cell in the same position in the tube and to reduce heat losses. The temperature profile was then the same in each experiment.

The spectrophotometer used was a Cary 17H spectrophotometer (Cary Instruments, Monrovia, CA). The signals from the spectrophotometer were recorded by a Kennedy Incremental 1600 magnetic tape recorder (Kennedy Co., Altadena, CA) via an interfacing unit.[9]

Chemicals. The chemicals used were $NdCl_3 \cdot 6H_2O$ (American Potash & Chemical Corp.), $GaCl_3$ (99.999% Riedel-de Haën, AG, Seelze-Hannover, West Germany; E. Merck, AG, Darmstadt, West Germany) and H_2SO_4 and NaCl (p.A., E. Merck, AG, Darmstadt, West Germany).

Neodymium trichloride was prepared by dehydrating $NdCl_3 \cdot 6H_2O$ in a stream of dry HCl prepared by reacting H_2SO_4 with NaCl. Finally, $NdCl_3$ was sublimed under vacuum at 700 °C.

Prior to use, $GaCl_3$ was distilled once through a quartz frit, without further purification.

Procedure. The procedure for charging the cells as described elsewhere[8] was followed with minor modifications. The absorption cells were cleaned in ethanol and distilled water, before residual carbon

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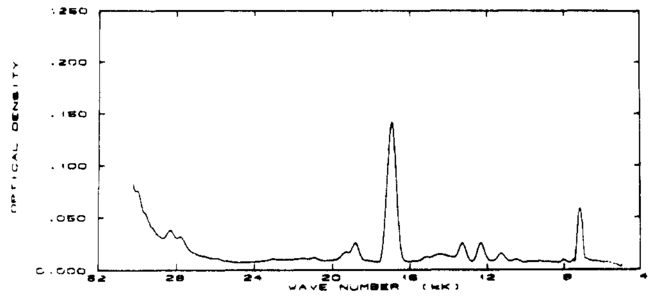

Figure 1. Spectrum of vapor phase in equilibrium with $NdCl_3(s)$ at $T_{min} = 801.8$ K and $P_{Ga_2Cl_6} = 5.168$ atm. T_{min} is the lowest temperature in the optical cell. The transition at 7 × 10^3 cm^{-1} is due to the window material of the cell.

impurities were burned away with a torch and removed with a stream of oxygen in the cell. Before charging, the cells were evacuated to less than 10^{-5} torr for several hours. The required amounts of salt were weighed out on a balance in the glovebox (H_2O content <1 ppm) and transferred to the cell through a side arm. For the molar absorption experiments the accurate weight of $NdCl_3$ was determined by differential weighing.

The vapor pressure of solid $GaCl_3$ is 4.5 torr at 68 °C,[10] and care has to be exercised in handling the salt and in charging the cells to avoid loss of $GaCl_3$. Gallium trichloride was transferred to a tube with a quartz frit. At one end of this tube the glass wall was made thin and easily breakable. The tubes containing $GaCl_3$ were first rapidly evacuated to 10^{-2}–10^{-3} torr and then refilled with $N_2(g)$ to 0.1 torr. The ampules were quickly sealed 15–20 cm away from the salt. The salt was then sublimed through the quartz frit into the thin-walled tube compartment, which was sealed off. In both steps, the thin tube was cooled in liquid nitrogen.

The thin-walled $GaCl_3$ ampule was transferred to the side arm of the absorption cell, where the ampule was broken after the side arm had been sealed off. Gallium trichloride was sublimed from the side arm into the cell, which was then sealed off close to the cell wall. One end of the optical cell was kept immersed in liquid nitrogen during the process. Molten gallium trichloride wets quartz, and when ampules containing $GaCl_3$ were crushed, it was not possible to distinguish glass splinters from $GaCl_3$ crystals. It is desirable to perform experiments at widely different dimer pressures in absorption spectroscopic studies of gas complex formation. The amount of glass splinters in the sample was determined by weighing in the glovebox. The unpredictable amount of glass did unfortunately result in a smaller variation of the Ga_2Cl_6 pressure than was planned.

No corrosion of the optical quartz cells was observed for this system, and equilibration times of 3 h were allowed before a spectrum was recorded after a change in temperature. The background spectrum has been subtracted in most experiments, and it was usually recorded below 100 °C, where absorption due to vapor complexes could not be detected.

The condensed phase in equilibrium with the vapor was solid above 600 K. One experiment was performed to investigate the solid phase. Neodymium trichloride and $GaCl_3$ were sealed in an evacuated quartz tube, which was placed in a quartz furnace and heated to 450 K. Neodymium trichloride dissolved in $GaCl_3(l)$ at this temperature, and the solid-phase appeared around 600 K. The tube was left at this temperature for 12 h, then one end was quenched in an ice–water mixture to condense $GaCl_3$, and the tube was opened in the glovebox. The X-ray powder diffraction pattern of the solid phase was identical with that of $NdCl_3$.

Results and Discussion

Molar Absorption Coefficient of the Nd–Ga–Cl Vapor Complex. A spectrum of the vapor phase in the $NdCl_3$–$GaCl_3$ system is shown in Figure 1. Three different experiments were carried out in order to determine the molar absorption coefficient of the Nd–Ga–Cl complex at 16.93 × 10^3 cm^{-1} in the temperature range 600–1000 K. Results calculated from eq 1 are given in Table I. For the three experiments, the mean values of the molar absorption coefficient are 22.4 ± 0.5, 20.8 ± 0.3, and 23.1 ± 0.4 L/(mol·cm). The differences in the molar absorptivities calculated from the three experiments are probably due to uncertainties in determination of the amount of $NdCl_3$. The mean value of the molar absorption coefficient calculated from all measurements is 22.0 ± 1.0 L/(mol·cm).

Table I. Molar Absorption Coefficients of the Nd–Ga–Cl Gas Complex at 16.93 × 10^3 cm^{-1}

specifications	T_{min}, K	A	ϵ, L/(mol·cm)	$\bar{\epsilon}$, L/(mol·cm)
expt no. 1: $P^\circ_{Ga_2Cl_6}$ = $(1.6799 \times 10^{-2})\overline{T}$, $m_{NdCl_3} = 1.08$ mg, $V = 34.64$ cm^3 $l = 20.00$ cm	613.5	0.0529	21.2	22.4 ± 0.5
	640.6	0.0548	22.0	
	668.9	0.0552	22.2	
	696.0	0.0560	22.5	
	710.8	0.0566	22.8	
	723.0	0.0564	22.7	
	739.1	0.0562	22.6	
	751.6	0.0564	22.7	
	765.1	0.0564	22.7	
	776.5	0.0564	22.7	
	799.0	0.0564	22.7	
expt no. 2: $P^\circ_{Ga_2Cl_6}$ = $(1.4211 \times 10^{-2})\overline{T}$, $m_{NdCl_3} = 0.80$ mg, $V = 32.18$ cm^3 $l = 20.00$ cm	619.6	0.0406	20.5	20.8 ± 0.3
	642.1	0.0406	20.5	
	669.5	0.0410	20.7	
	696.4	0.0414	20.9	
	709.3	0.0418	21.1	
	723.8	0.0410	20.7	
	737.1	0.0418	21.1	
	752.3	0.0414	20.9	
	778.3	0.0418	21.1	
	798.3	0.0414	20.9	
	820.8	0.0414	20.9	
	844.6	0.0420	21.1	
	871.3	0.0402	20.3	
	898.6	0.0410	20.6	
	909.4	0.0404	20.4	
	926.4	0.0410	20.7	
	937.7	0.0410	20.7	
	952.6	0.0412	20.8	
	973.1	0.0417	21.0	
	995.5	0.0422	21.3	
expt no. 3: $P^\circ_{Ga_2Cl_6}$ = $(1.5884 \times 10^{-2})\overline{T}$, $m_{NdCl_3} = 1.14$ mg, $V = 33.72$ cm^3 $l = 20.00$ cm	616.7	0.0617	22.9	23.1 ± 0.4
	641.6	0.0615	22.8	
	665.7	0.0619	22.9	
	690.7	0.0617	22.9	
	715.6	0.0617	22.9	
	740.9	0.0617	22.9	
	760.9	0.0619	22.9	
	785.4	0.0619	22.9	
	803.4	0.0617	22.9	
	822.7	0.0619	22.9	
	832.4	0.0621	23.0	
	845.7	0.0619	22.9	
	861.0	0.0626	23.2	
	868.2	0.0628	23.3	
	877.2	0.0629	23.3	
	893.5	0.0637	23.6	
	910.5	0.0643	23.8	
	925.3	0.0653	24.2	

For the Nd–Al–Cl vapor complex, Øye and Gruen[5] detected a 0.02 × 10^3 cm^{-1} change in the location of the absorption maximum around 17 × 10^3 cm^{-1}. The strongest absorption band for the Nd–Ga–Cl complex shifts from 16.98 × 10^3 to 16.87 × 10^3 cm^{-1} when the temperature is increased from 600 to 900 K. Thus, the wavenumber 16.93 × 10^3 cm^{-1} is a mean value for the band position. Two of the experiments indicate a weakly increasing molar absorption coefficient at temperatures above 800–900 K, and recent experiments[11] at higher temperatures have verified this. Higher molar absorption coefficients and shifts in band location with increasing temperature are probably due to equilibria involving two or more vapor complexes with different molecular structures.

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Table II. Molar Absorption Coefficient of Nd–Ga–Cl Vapor Species in Equilibrium with $GaCl_3(g)$ and $NdCl_3(s)$ at T_{min} = 801.8 K and $P_{Ga_2Cl_6}$ = 5.168 atm

wavenumber, 10^3 cm^{-1}	11.25	12.30	13.27	16.93	18.75	19.30	27.80	28.32
ϵ, L/(mol·cm)	1.3	3.1	2.8	22.0	3.0	1.3	1.8	2.0

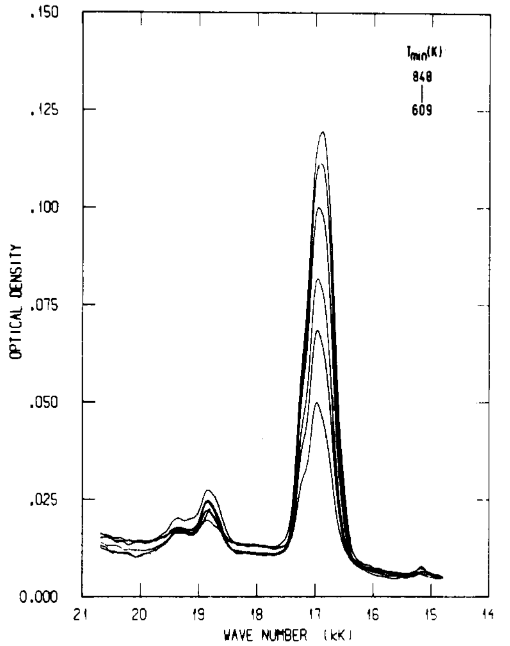

Figure 2. Experiment 9, the Nd–Ga–Cl gas complex in equilibrium with $NdCl_3(s)$ and $Ga_2Cl_6(g)$ (T_{min} (K) = 609.6, 662.7, 702.1, 753.7, 803.9, 848.2).

The small temperature variation of the molar absorptivity at 16.93 × 10^3 cm^{-1} was neglected, and the mean value 22.0 L/(mol·cm) was used to calculate partial pressures of the Nd–Ga–Cl vapor complex at all temperatures and total pressures. When this is done, it is assumed that if more than one gas complex is formed, all complex species have the same molar absorption coefficient. Further implications of this assumption have been discussed by Øye and Gruen.[5] The molar absorption coefficient of the Nd–Ga–Cl gas complex at 16.93 × 10^3 cm^{-1} is slightly higher than for the corresponding transition in the Nd–Al–Cl vapor complex, which is 18.8 L/(mol·cm).[5]

The remaining transitions shown in Figure 1 had optical densities too low to permit a direct determination of their molar absorption coefficients. The molar absorption coefficient for these transitions were hence calculated from experiments where a condensed phase was present and where the partial pressure of the complex had been calculated by using the molar absorption coefficient for the transition at 16.93 × 10^3 cm^{-1}. The results are given in Table II and are close to the molar absorption coefficients reported for the corresponding transitions of the Nd–Al–Cl complex.[5]

Experiments with the Gas Phase in Equilibrium with a Condensed Phase. Six experiments with condensed $NdCl_3$ present were performed in the temperature range 600–1150 K. Below approximately 600 K $NdCl_3(s)$ dissolves in molten $GaCl_3$, and a detailed study of the complex formation below 600 K was not undertaken.

Spectra recorded between 14.7 and 20.8 × 10^3 cm^{-1} are shown in Figure 2. At 17.2 × 10^3 cm^{-1} a shoulder is noticed, which becomes difficult to observe at higher temperatures. A similar shoulder was observed by Banks et al.[12] and Johnson and Sandoe[13] for Nd^{3+} in molten LiCl–KCl mixtures. The band at 16.93 × 10^3 cm^{-1} shifts 0.22 × 10^3 cm^{-1} to the red when the temperature increases from 575 to 1168 K. These observations indicate formation of more than one gaseous complex. Partial pressures of the complex species calculated

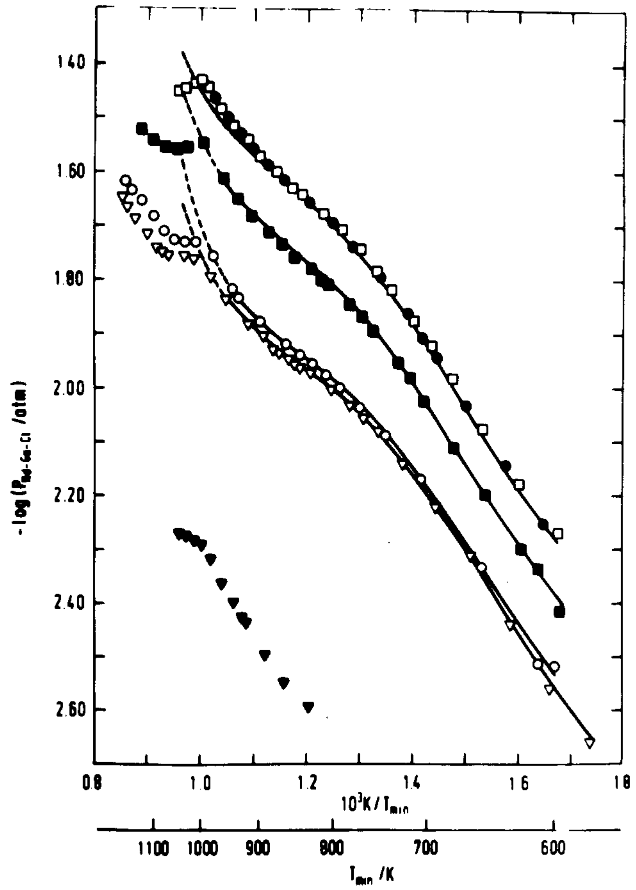

Figure 3. Logarithm of the total complex pressure vs. 10^3 K/T_{min}: (▼) experiment 4; (▽) experiment 5; (○) experiment 7; (■) experiment 9; (●) experiment 8; (□) experiment 6. Fully drawn lines are those of the model (n_1 = 0.5, n_2 = 1.5, n_3 = 2.0) fit to the data. Dashed lines are extrapolations outside the region of the model.

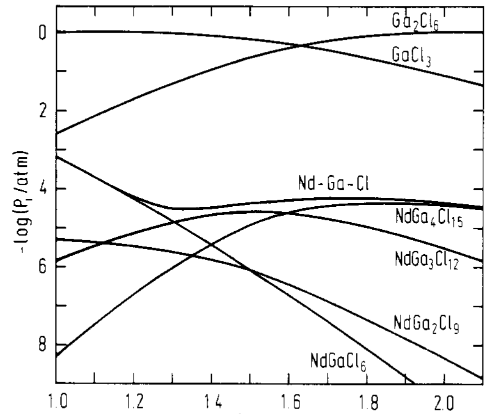

Figure 4. Temperature variation of the partial pressures of the complex gas species for 1 atm of total pressure for the four-species model. Nd–Ga–Cl denotes the total pressure of the complexes.

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Table III. Partial Pressure P_c of Nd–Ga–Cl Gas Complexes Calculated from Measured Optical Density at 16.93×10^3 cm^{-1}

specifications	T_{min}, K	$10^3/T_{min}$, K^{-1}	$\bar{T}$, K	$P^\circ_{Ga_2Cl_6}$, atm	$P_{Ga_2Cl_6}$, atm	A	$10^3 P_c$, atm
expt no. 4: $V = 73.68$ cm^3, $l = 15.16$ cm, $m_{NdCl_3} = 45.5$ mg, $m_{GaCl_3} = 1.6560$ g	828.6	1.207	847.6	4.439	1.232	0.0122	2.544
	864.8	1.156	883.8	4.628	0.945	0.0130	2.827
	891.8	1.121	910.8	4.770	0.773	0.0142	3.182
	919.4	1.088	938.4	4.815	0.624	0.0158	3.648
	928.9	1.077	947.9	4.865	0.579	0.0160	3.731
	940.2	1.064	959.2	5.023	0.529	0.0170	4.012
	961.6	1.040	980.6	5.135	0.448	0.0179	4.318
	980.6	1.020	999.6	5.235	0.386	0.0195	4.796
	997.2	1.003	1016.2	5.322		0.0203	5.079
	1014.5	0.986	1033.5	5.412		0.0204	5.187
	1031.2	0.970	1050.2	5.500		0.0205	5.297
	1046.7	0.955	1065.7	5.581		0.0205	5.375
expt no. 5: $V = 32.41$ cm^3, $l = 20.00$ cm, $m_{NdCl_3} = 0.1345$ g, $m_{GaCl_3} = 1.3034$ g	575.2	1.739	580.2	5.437	5.044	0.0202	2.186
	602.1	1.661	607.1	5.689	5.095	0.0244	2.762
	630.4	1.586	635.4	5.954	5.076	0.0307	3.638
	666.1	1.501	671.1	6.289	4.932	0.0398	4.981
	689.3	1.451	694.3	6.506	4.765	0.0437	5.658
	693.1	1.443	698.1	6.542	4.732	0.0462	6.015
	722.5	1.348	727.5	6.817	4.430	0.0532	7.218
	748.6	1.336	753.6	7.015	4.098	0.0590	8.237
	764.3	1.308	769.3	7.162	3.877	0.0611	8.709
	778.9	1.284	783.9	7.299	3.660	0.0630	9.151
	800.8	1.249	805.8	7.504	3.322	0.0662	9.886
	827.8	1.208	832.8	7.757	2.902	0.0686	10.590
	841.9	1.188	846.9	7.936	2.686	0.0690	10.898
	848.4	1.179	853.4	7.997	2.589	0.0694	11.045
	855.3	1.169	860.3	8.061	2.487	0.0703	11.279
	866.1	1.155	871.1	8.163	2.332	0.0699	11.355
	876.1	1.141	881.1	8.256	2.193	0.0709	11.650
	892.0	1.121	897.0	8.405	1.983	0.0759	12.696
	920.8	1.086	939.8	8.806	1.682	0.0771	13.513
	952.2	1.050	971.2	9.101	1.358	0.0809	14.652
	980.2	1.020	999.2	9.363		0.0880	16.398
	1009.8	0.990	1028.8	9.640		0.0929	17.823
	1032.9	0.968	1051.9	9.857		0.0901	17.675
	1060.2	0.943	1079.2	10.113		0.0888	17.872
	1071.3	0.933	1090.3	10.217		0.0886	18.015
	1085.0	0.922	1104.0	10.345		0.0890	18.323
	1110.6	0.900	1129.6	10.585		0.0923	19.444
	1136.0	0.880	1155.0	10.823		0.0970	20.893
	1155.3	0.866	1174.3	11.004		0.1002	21.943
	1167.8	0.856	1186.8	11.121		0.1026	22.708
expt no. 6: $V = 32.25$ cm^3, $l = 20.00$ cm, $m_{NdCl_3} = 0.2017$ g, $m_{GaCl_3} = 1.7976$ g	597.5	1.674	602.5	7.803	7.163	0.0477	5.360
	625.0	1.600	630.0	8.159	7.204	0.0564	6.626
	652.2	1.533	657.2	8.512	7.151	0.0682	8.359
	676.3	1.479	681.3	8.824	7.019	0.0817	10.380
	679.8	1.471	684.8	8.869	6.993	0.0825	10.536
	696.4	1.436	701.4	9.084	6.846	0.0915	11.968
	713.2	1.402	718.2	9.302	6.659	0.0990	13.260
	735.2	1.360	740.2	9.587	6.358	0.1097	15.143
	751.1	1.331	756.1	9.793	6.106	0.1164	16.413
	767.5	1.303	772.5	10.005	5.819	0.1239	17.849
	790.6	1.265	795.6	10.304	5.378	0.1322	19.614
	812.3	1.231	817.3	10.585	4.938	0.1377	20.988
	838.6	1.193	843.6	10.926	4.391	0.1444	22.717
	838.7	1.192	843.7	10.927	4.389	0.1438	22.625
	852.4	1.173	871.4	11.286	4.203	0.1436	23.336
	876.7	1.141	895.7	11.601	3.703	0.1495	24.972
	899.3	1.112	918.3	11.893	3.263	0.1562	26.749
	921.1	1.086	940.1	12.176	2.870	0.1639	28.734
	942.8	1.061	961.8	12.457	2.514	0.1692	30.348
	964.5	1.037	983.5	12.738	2.195	0.1780	32.647
	986.1	1.014	1005.1	13.017	1.914	0.1905	35.708
	999.1	1.001	1018.1	13.186		0.1933	36.700
	1011.5	0.989	1030.5	13.346		0.1886	36.244
	1028.6	0.972	1047.6	13.568		0.1819	35.537
	1045.4	0.957	1064.4	13.785		0.1767	35.074
expt no. 7: $V = 36.27$ cm^3, $l = 20.00$ cm, $m_{NdCl_3} = 0.1684$ g, $m_{GaCl_3} = 1.4996$ g	599.1	1.669	604.1	5.820	5.243	0.0239	2.693
	611.3	1.636	616.3	5.937	5.249	0.0266	3.057
	653.2	1.531	658.2	6.341	5.155	0.0376	4.615
	706.7	1.415	711.7	6.856	4.756	0.0503	6.676
	726.2	1.377	731.2	7.044	4.677	0.0427	5.823
	742.6	1.347	747.6	7.202	4.326	0.0583	8.128
	768.5	1.301	773.5	7.452	3.955	0.0629	9.073
	792.3	1.262	797.3	7.681	3.587	0.0671	9.977

Table III (*Continued*)

specifications	T_{min}, K	$10^3/T_{min}$, K^{-1}	$\bar{T}$, K	$P°_{Ga_2Cl_6}$, atm	$P_{Ga_2Cl_6}$, atm	A	10^3P_c, atm
	807.9	1.238	812.9	7.831	3.338	0.0700	10.612
	824.4	1.213	829.4	7.990	3.047	0.0717	11.090
	841.6	1.188	846.6	8.156	2.804	0.0731	11.541
	859.1	1.164	864.1	8.324	2.537	0.0748	12.054
	879.9	1.136	884.9	8.525	2.237	0.0759	12.525
	906.8	1.103	911.8	8.784	1.885	0.0781	13.280
	933.9	1.071	938.9	9.045	1.574	0.0840	14.708
	942.8	1.061	961.8	9.266	1.519	0.0851	15.264
	975.5	1.025	994.5	9.581		0.0947	17.563
	1008.6	0.991	1027.6	9.900		0.0970	18.588
	1030.7	0.970	1049.7	10.112		0.0947	18.538
	1052.6	0.950	1071.6	10.323		0.0935	18.685
	1070.8	0.934	1089.8	10.499		0.0942	19.145
	1092.2	0.916	1111.2	10.705		0.0937	19.417
	1119.8	0.893	1138.8	10.971		0.0984	20.897
	1135.0	0.881	1154.0	11.117		0.1012	21.779
	1149.3	0.870	1168.0	11.255		0.1055	22.986
	1167.5	0.857	1186.5	11.430		0.1086	24.030
expt no. 8: $V = 35.04$ cm^3, $l = 20.00$ cm, $m_{NdCl_3} = 0.1626$ g, $m_{GaCl_3} = 1.9571$ g	607.2	1.647	612.2	7.967	7.203	0.0487	5.560
	634.7	1.576	639.2	8.319	7.213	0.0602	7.176
	664.1	1.506	669.1	8.708	7.112	0.0739	9.221
	691.6	1.446	696.6	9.066	6.908	0.0873	11.341
	704.3	1.420	709.3	9.231	6.779	0.0933	12.341
	719.0	1.391	724.0	9.422	6.601	0.1012	13.664
	746.7	1.339	751.7	9.783	6.194	0.1146	16.065
	775.3	1.290	780.3	10.155	5.689	0.1249	18.175
	801.8	1.247	806.8	10.500	5.168	0.1343	20.206
	802.6	1.246	807.6	10.510	5.151	0.1347	20.287
	815.9	1.226	820.9	10.683	4.878	0.1368	20.942
	829.3	1.206	834.3	10.858	4.598	0.1406	21.875
	849.1	1.178	868.1	11.297	4.285	0.1430	23.150
	851.7	1.174	856.7	11.149	4.132	0.1466	23.421
	865.3	1.156	884.3	11.508	3.947	0.1460	24.077
	887.6	1.127	906.6	11.799	3.498	0.1515	25.614
	909.2	1.100	928.2	12.080	3.090	0.1580	27.349
	930.2	1.075	949.2	12.353	2.725	0.1657	29.331
	952.8	1.050	971.8	12.647	2.370	0.1745	31.624
	974.8	1.026	993.8	12.933	2.088	0.1858	34.434
	996.4	1.004	1015.4	13.214	1.799	0.1925	36.452
	1017.8	0.983	1036.8	13.493		0.1860	35.963
	1034.8	0.966	1053.8	13.714		0.1815	35.668
expt no. 9: $V = 36.28$ cm^3, $l = 20.00$ cm, $m_{NdCl_3} = 54.9$ mg, $m_{GaCl_3} = 1.8206$ g	595.2	1.680	600.2	7.018	6.414	0.0343	3.839
	609.6	1.640	614.6	7.186	6.440	0.0404	4.630
	622.2	1.607	627.2	7.334	6.445	0.0430	5.030
	637.0	1.570	642.0	7.507	6.426	0.0503	6.022
	649.6	1.539	654.6	7.654	6.389	0.0520	6.348
	662.7	1.509	667.7	7.807	6.329	0.0602	7.496
	675.8	1.480	680.8	7.960	6.247	0.0618	7.846
	702.1	1.424	707.1	8.268	6.014	0.0715	9.428
	714.6	1.399	719.6	8.414	5.874	0.0783	10.508
	728.0	1.374	733.0	8.571	5.703	0.0814	11.127
	753.7	1.327	758.7	8.871	5.322	0.0907	12.833
	766.4	1.305	771.4	9.020	5.113	0.0947	13.623
	780.8	1.281	785.8	9.188	4.861	0.0972	14.244
	803.9	1.244	808.9	9.458	4.437	0.1030	15.537
	814.9	1.227	819.9	9.587	4.229	0.1033	15.795
	827.1	1.209	832.1	9.729	3.997	0.1071	16.619
	848.2	1.179	853.2	9.976	3.599	0.1095	17.423
	868.2	1.152	873.2	10.210	3.232	0.1136	18.499
	899.4	1.112	918.4	10.738	2.765	0.1128	19.319
	922.1	1.084	941.1	11.004	2.406	0.1182	20.744
	943.0	1.060	962.0	11.248	2.107	0.1240	22.246
	965.8	1.035	984.8	11.515	1.819	0.1324	24.316
	994.3	1.006	1013.3	11.848	1.510	0.1499	28.326
	1024.9	0.976	1043.9	12.206		0.1416	27.566
	1044.9	0.957	1063.9	12.440		0.1381	27.399
	1072.1	0.933	1091.1	12.758		0.1357	27.612
	1098.6	0.910	1117.6	13.068		0.1369	28.532
	1126.4	0.888	1145.4	13.393		0.1408	30.075

from eq 2 are given in Table III and are plotted vs. reciprocal temperature in Figure 3.

The treatment of the data is similar to that for the $NdCl_3$–$AlCl_3$ system.[5] When it is assumed that complexes with only one Nd^{3+} ion are formed, the complex formation reactions may generally be formulated

$$NdCl_3(s) + n_iGa_2Cl_6(g) = NdGa_{2n_i}Cl_{6n_i+3}(g) \qquad (5)$$

Table IV. Results from Fit of the Model Equation (7) to Experimental Partial Pressures of the Nd-Ga-Cl Complex with Data from Experiments 5–9

n_1	n_2	n_3	n_4	species	ΔH°_i, kJ/mol	ΔS°_i, J/(mol·K)	% σ_{total}
0.5				$NdGaCl_6$	84.1	52.4	10.6
	2.0			$NdGa_4Cl_{15}$	36.6	−16.3	
		...					
			...				
0.5				$NdGaCl_6$	135.9	104.9	9.4
	1.0			$NdGa_2Cl_9$	76.5	24.0	
		2.0		$NdGa_4Cl_{15}$	41.2	−9.0	
			...				
0.5				$NdGaCl_6$	146.6	109.1	2.8
	1.0			$NdGa_2Cl_9$	105.9	52.2	
		1.5		$NdGa_3Cl_{12}$	65.2	24.6	
			2.0	$NdGa_4Cl_{15}$	20.9	−43.1	
0.5				$NdGaCl_6$	135.0	98.7	2.9
	1.5			$NdGa_3Cl_{12}$	55.9	15.1	
		2.0		$NdGa_4Cl_{15}$	8.5	−65.3	
			...				
1.0				$NdGa_2Cl_9$	61.0	27.6	10.4
	2.0			$NdGa_4Cl_{15}$	8.6	−62.8	
		...					
			...				
1.0				$NdGa_2Cl_9$	99.3	59.0	8.8
	1.5			$NdGa_3Cl_{12}$	55.4	15.1	
		2.0		$NdGa_4Cl_{15}$	9.0	−66.5	
			...				

By comparison of individual experiments n_i was found to vary between 2.16 and 0.85. The pressure of the dimer, $P_{Ga_2Cl_6}$, was calculated by the ideal gas law with use of the weighed-in amount of $GaCl_3$ with correction for the amount consumed in the complexing and dissociation reactions (5) and (6). An

$$\begin{gathered} Ga_2Cl_6(g) = 2GaCl_3(g) \\ \log K\,(\text{atm}) = -4595/T + 7.066 \end{gathered} \qquad (6)$$

average value of $n = 1.62$ was used to perform the minor correction due to $GaCl_3$ bound in the complex while the equilibrium constants of Fischer and Jübermann[10] were used for corrections due to the dissociation shown in eq 6.

The experimental data were fitted to different thermodynamical models, with the least-squares sum minimized:

$$F = \sum[[P_{\text{Nd-Ga-Cl}}(\text{exptl}) - \sum_i P_{Ga_2Cl_6}{}^{n_i} \exp(\Delta S^\circ_i/R - \Delta H^\circ_i/RT)] \times 100/P_{\text{Nd-Ga-Cl}}(\text{exptl})]^2 \qquad (7)$$

The last term in the numerator is the total pressure of neodymium complexes calculated from the model equation, with different combinations of $n_i = 0.5$, 1.0, 1.5, and 2.0 chosen. A computer program developed by Hertzberg[14] was used. A species with $n_i = 2.0$ was always included in order to account for the low-temperature complexation. All combinations with three or two species were tried, with use of $n_i = 1.5$, 1.0, and 0.5 for the other species. In Table IV the results for the different choices of stoichiometric coefficients are given together with the percent standard deviation in fit; ΔH°_i and ΔS°_i are the enthalpy and entropy of the complex formation reactions (eq 5).

With $n_1 = 0.5$, $n_2 = 1.5$, and $n_3 = 2.0$, which correspond to the gas species $NdGaCl_6$, $NdGa_3Cl_{12}$, and $NdGa_4Cl_{15}$, respectively, the model gives the best three-species fit to the experimental data. In experiment 4, some $GaCl_3$ was lost during charging of the cell and hence the results from this experiment have been omitted from the calculations. When this experiment is included, only small changes for the values of ΔH°_i and ΔS°_i result, but the standard deviation in fit for the 0.5–1.5–2.0 model increases to 5.0%, which still is better than any of the other choices of n_1, n_2, and n_3.

In spite of the fact that a three-species model gave a very satisfactory description of the data, a four-species model that also included $NdGa_2Cl_9$ was tried, as there appears to be no principal reason for the absence of this species. A straightforward fit gave a standard deviation of 2.9% but showed a 99% coupling between ΔH°_2 and ΔS°_2. In order to remedy this, the restriction $\Delta H^\circ_2 = {}^1/_2(\Delta H^\circ_1 + \Delta H^\circ_3)$ was introduced and the results given in Table IV were obtained. The temperature variation for the concentration of complexes for the four-species model is depicted in Figure 4 for a total pressure of 1 atm. The figure shows that the low-molecular-weight complex $NdGaCl_6$ is dominant at high temperatures while $NdGa_4Cl_{15}$ is the most abundant species below 350 °C at 1 atm total pressure. The shift in equilibrium between $NdGa_4Cl_{15}$ and $NdGa_3Cl_{12}$, which is the dominating vapor complex in an intermediate temperature range, results in the weakly S-shaped curves between 600 and 700 K in Figure 3. A similarly shaped curve of $\log P_c$ vs. $1/T$ has been observed by Sørlie and Øye[15] for gas complexation between $TiCl_3$ and Al_2Cl_6. Due to pressure and temperature effects on the dissociation of Ga_2Cl_6, the partial pressure of species like $NdGa_4Cl_{15}$, $NdGa_3Cl_{12}$, and $NdGa_2Cl_9$ reaches a maximum at a certain temperature. The position of the maximum depends on the total pressure of $GaCl_3$ and shifts to higher temperatures with increasing total pressure. The changed curvature between 880 and 1000 K in Figure 3 is due to the relatively high partial pressure of $NdGaCl_6$ and $NdGa_2Cl_9$ in this temperature range. Figure 4 shows that $NdGa_2Cl_9$ never becomes a dominant species, a result which is to be expected from the model calculation given in Table IV. In Figure 3 a maximum is observed around 1000 K and is due to the melting of $NdCl_3$ in a $GaCl_3$ atmosphere. This causes a decrease in the activity of $NdCl_3$ and hence a lowered partial pressure of the complexes relative to that for the solid–gas case. The activity of $NdCl_3$ or the composition of the liquid phase is not known, and only

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data recorded below 1000 K have been used in the model calculations.

The thermodynamics of the Nd–Ga–Cl and Nd–Al–Cl[5] complexes with the same stoichiometry are similar. It is interesting to note that the difference in the enthalpies or entropies for the formation of the Nd–Al–Cl and Nd–Ga–Cl complexes per 0.5 M'_2Cl_6 molecule (M′ = Al, Ga) is nearly constant in the sequence $NdM'Cl_6$–NdM'_3Cl_{12}–NdM'_4Cl_{15}. The importance of retaining the coordination number of the central transition-metal ion M in MAl_2Cl_8(g) as in the solid transition-metal chloride has been pointed out in the literature.[5,16] In the proposed structure for $LnAl_3Cl_{12}$ (Ln = Nd, Sm), three $AlCl_4$ tetrahedra are bound by a face to the lanthanide ion,[5,16] thus giving Nd^{3+} a coordination number of 9 as in $NdCl_3$(s). The complex $LnAl_4Cl_{15}$(g) would then consist of two $AlCl_4$ groups and one Al_2Cl_7 group, whereas the lower molecular weight complexes can be thought of as being formed by gradually removing $AlCl_3$ groups as the temperature is increased. This agrees with the constant difference found for the enthalpy and entropy of formation for the Nd–Ga–Cl and Nd–Al–Cl[5] complexes and suggests similar structures of the gas complexes, in which the same type and number of bonds are formed. Stepwise formation of vapor complexes between transition-metal dichlorides and $M'Cl_3$ (M′ = Fe, Al, Ga, In) has been discussed by Dienstbach and Emmenegger.[17,18] Over most of the studied temperature range, where $NdGa_3Cl_{12}$(g) and $NdGa_4Cl_{15}$(g) are the dominating complex species, a constant molar absorption coefficient would be expected. In these two complexes the coordination number of Nd^{3+} is probably the same. At high temperatures, where the lower molecular weight species $NdGa_2Cl_9$(g) and $NdGaCl_6$(g) are abundant, the coordination number of Nd^{3+} is lower and an increasing molar absorption coefficient is hence conceivable.

Although it is not conclusive with respect to structure, the empirical bond energy model of Hastie[2] reproduces our value for $\Delta H^\circ{}_1$ if Nd^{3+} is coordinated by four chloride ions (where two bridge to Ga) and corrections for the change in cation–cation repulsive potential energy are applied.

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Registry No. $NdGaCl_6$, 87585-73-7; $NdGa_2Cl_9$, 87566-85-6; $NdGa_3Cl_{12}$, 87566-86-7; $NdGa_4Cl_{15}$, 79747-67-4; $NdCl_3$, 10024-93-8; $GaCl_3$, 13450-90-3.

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Cobalt(III) Complex of Glycylglycyl-L-histidine: Preparation, Characterization, and Conformation

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A diamminecobalt(III) complex of glycylglycyl-L-histidine has been prepared in which the NH_2 group, two deprotonated peptide nitrogens, and the imidazole group are coordinated. The circular dichroism, UV–visible, and ^1H and ^{13}C NMR spectra of the complex are presented. The six-membered diamine chelate ring is exclusively in a puckered conformation with the carboxylate group in an axial orientation. The pK_a values at 298 K for the complex are as follows: coordinated imidazole NH, 9.81 ± 0.3; carboxylate, 4.06 ± 0.03 (with ^2H, 3.82).

Introduction

There has been intense interest in recent years in the tripeptide glycylglycyl-L-histidine as a model for the copper(II) binding site of albumin, the transport protein for copper(II) in blood. The N-terminal portion, Asp-Ala-His, of albumin binds copper(II) strongly in a square-planar complex involving the α-amino group of the aspartic acid residue, an imidazole nitrogen of the histidine, and two intervening deprotonated peptide nitrogens.[1-3] As Gly-Gly-His contains the same potential metal binding sites, there have been extensive studies of the interaction of this tripeptide with labile metal ions, principally copper(II) and nickel(II).[4-14] At physiological pH, the predominant species in solution is believed to be $[M(H_{-2}GGHis)]^-$ with the above mode of coordination.[15] A crystal structure of the copper(II) complex of the methylamide of Gly-Gly-L-His has confirmed this structure.[16] Compared to the copper(II) complexes of simple tripeptides, coordination of the imidazole group leads to large differences in the stability, in the pH response, in the electronic spectrum, and in the kinetic behavior of the copper(II) complex.[7]

In the present study, the coordination of Gly-Gly-L-His to the inert metal ion cobalt(III) is examined. The synthesis of $[Co(NH_3)_2(H_{-2}GGHis)]$ (Figure 1) is reported and its structure characterized by various spectroscopic techniques. The X-ray structures of a number of complexes of histidine peptides have the six-membered chelate ring formed by coordination of the imidazole nitrogen and the adjacent peptide nitrogen in a conformation with the terminal carboxylate group

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