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Molecular structure of $GdCl_3$. Nuclear dynamics of the trichlorides of Gd, Tm, and Lu

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The structure of gadolinium trichloride has been studied by joint gas-phase electron diffraction and mass spectrometry at $T = 1160$ K. The following thermal-average parameters have been determined: $r_g(\text{Gd–Cl}) = 247.4(5)$, $r_g(\text{Cl}\cdots\text{Cl}) = 422.0(16)$, $l_g(\text{Gd–Cl}) = 9.6(1)$, $l_g(\text{Cl}\cdots\text{Cl}) = 33.3(12)$ pm, Cl–Gd–Cl 117.0(11)°. A dynamic model taking into account the out-of-plane bending vibration anharmonicity was applied in the analysis. Previously obtained experimental data for $LuCl_3$ and $TmCl_3$ were also reanalysed using this model. Analysis in terms of the dynamic model indicates that $GdCl_3$, $LuCl_3$, and $TmCl_3$ all have planar (D_{3h}) equilibrium structures.

Introduction

The first gas-phase electron diffraction (GED) experimental data on $GdCl_3$ structure were obtained in 1977[1] at $T = 1300$–1350 K. The structure analysis yielded the following parameters: $r_g(\text{Gd–Cl}) = 248.9(6)$, $r_g(\text{Cl}\cdots\text{Cl}) = 415.0(43)$ pm, Cl–Gd–Cl 113°, thus corresponding to a pyramidal structure of C_{3v} symmetry. The equilibrium structure of $GdCl_3$ was also assumed to be pyramidal. The vapour composition during the experiment was not determined; therefore the structure refinement was performed under the assumption that the vapour contained only the monomer. The temperature of the first experiment was about 200 K higher than that of the present experiment. According to the vapour composition dependence on the temperature[2] the dimeric content was probably significantly higher than in the present work, thus resulting in an inaccuracy in the structure parameters. Selivanov *et al.*[3] investigated the gas-phase infrared spectrum of $GdCl_3$ and assigned the band at 326 cm^{-1} to the ν_3 vibrational frequency. In 1975 Perov *et al.*[4] studied the matrix-isolation absorption spectrum and established the assignments for three vibrational frequencies (ν_2 53, ν_3 318, ν_4 82 cm^{-1}). No bands that could be assigned to the ν_1 vibrational frequency were observed in either spectroscopic study and the authors supposed the valence angle to be close to 120° which corresponds to a planar D_{3h} equilibrium structure. The latest *ab initio* calculations[5–7] yielded a planar D_{3h} structure for all trichlorides of the lanthanides.

Experimental

A synchronous gas-phase electron diffraction and mass spectrometric experiment was carried out on a modified EMR-100/APDM-1 unit.[8,9] A sample was evaporated at 1160 K from a molybdenum cell with a cylindrical effusion nozzle of 0.6 × 1.0 mm (diameter × length). Mass spectra were recorded at an ionization voltage of 50 V. The spectral data of the vapor over $GdCl_3$ are presented in Table 1. It was assumed that the $Gd_2Cl_5^+$ ion originated from dimeric molecules, while the other ions came from the monomer. The ratio of the ionization cross-sections of Gd_2Cl_6 and $GdCl_3$ was assumed to be 2 : 1; thus the dimer concentration was less than 1%.

Electron diffraction patterns were obtained for camera distances $L_a = 338$ and 598 mm at an accelerating voltage of 72.5 kV. The wavelength of the electrons was calibrated using crystalline ZnO powder. Optical densities were measured by a modified computer controlled MD-100 microdensitometer. Six plates from each camera distance were used in the processing.

Conventional structure refinement

A least-squares structure refinement was performed using a modified version of the KCED program.[10] It was postulated that the molecule in question has a third order symmetry axis and has either C_{3v} or D_{3h} symmetry. Internuclear distances $r_a(\text{Gd–Cl})$ and $r_a(\text{Cl}\cdots\text{Cl})$, r.m.s. amplitudes $l_a(\text{Gd–Cl})$ and $l_a(\text{Cl}\cdots\text{Cl})$, and the asymmetry constant k of the Gd–Cl bond were treated as independent parameters. The Gd_2Cl_6 content was found to be too low for reliable determination of the dimeric structure; therefore the final structure refinement was carried out by assuming that only the monomer was present. The results of structure refinement of $sM(s)$ curves obtained from the long and short camera distances as well as for the joint processing of both curves are presented in Table 2. The experimental and calculated molecular intensity curves and the difference curves are shown in Fig. 1, the experimental and calculated radial distribution curves and difference curve multiplied by 2 in Fig. 2.

The thermal-average structural parameters of $GdCl_3$ along with previously obtained $LuCl_3$ and $TmCl_3$ data[11,12] are presented in Table 3.

Table 1 Mass spectral data (m/z) of the vapour over $GdCl_3$. Nozzle temperature 1166 K, ionizing electron energy 50 eV

Gd^+	$GdCl^+$	$GdCl_2^+$	$GdCl_3^+$	$Gd_2Cl_5^+$	Gd^{2+}	$GdCl^{2+}$	$GdCl_2^{2+}$	$GdCl_3^{2+}$
49.7	23.5	100	7.5	1.7	21.0	7.2	4.7	61.3

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Table 2 Structure refinement results for gadolinium trichloride[a]

$s_{min} - s_{max}$/nm^{-1}	r_a(Gd–Cl)/pm	r_a(Cl···Cl)/pm	l_a(Gd–Cl)/pm	l_a(Cl···Cl)/pm	k(Gd–Cl)/pm^3	R_f (%)
18–141	247.06(5)	420.1(8)	9.75(9)	32.7(7)	0[b]	2.90
24–247	247.04(5)	418.7(6)	9.55(4)	33.6(4)	29(4)	3.32
18–247	247.05(5)	419.4(5)	9.63(4)	33.3(4)	19(4)	3.34

[a] σ_{LS} given in parentheses. [b] Fixed, cannot be determined.

Table 3 Thermal-average parameters of lanthanide trichlorides[a]

Ln	r_g(Ln–Cl)/pm	r_g(Cl···Cl)/pm	l_g(Ln–Cl)/pm	l_g(Cl···Cl)/pm	Cl–Ln–Cl/°	δ(Cl···Cl)[b]/pm	T/K
Gd	247.4(5)	422.0(16)	9.6(1)	33.3(12)	117.0(11)	6.5(18)	1160(10)
Tm	242.2(6)	411.3(21)	8.9(2)	30.8(18)	116.2(14)	8.2(23)	1123(20)
Lu	240.3(5)	411.9(18)	8.6(2)	31.5(11)	117.9(13)	4.4(20)	1070(10)

[a] Estimated total errors shown in parentheses were calculated by the following formulae: $\sigma = [(2.5\sigma_{LS})^2 + \sigma_{SC}{}^2]^{1/2}$ for distances (r_g), $\sigma = 3\sigma_{LS}$ for amplitudes (l_g). [b] Shrinkage $\delta(\mathrm{Cl}\cdots\mathrm{Cl}) = \sqrt{3}r_g(\mathrm{Lu–Cl}) - r_g(\mathrm{Cl}\cdots\mathrm{Cl})$.

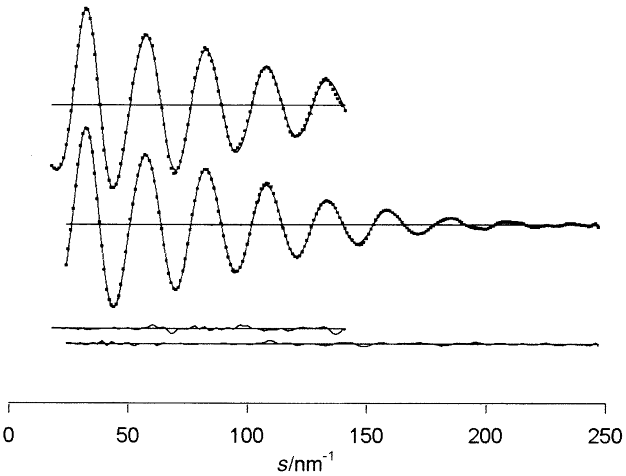

Fig. 1 Experimental (squares) and theoretical (lines) molecular intensity curves and difference curves (below) of $GdCl_3$.

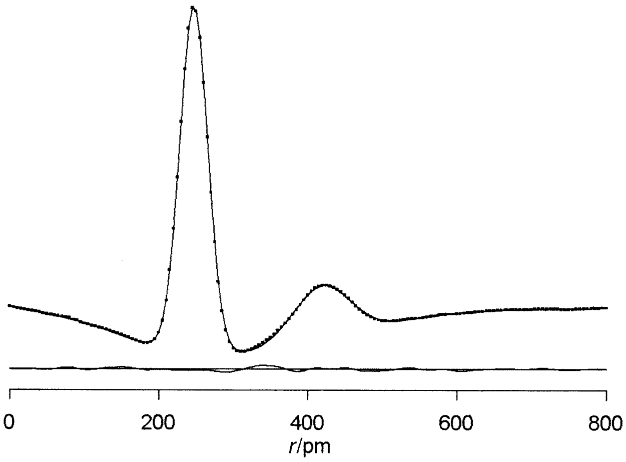

Fig. 2 Experimental (squares) and calculated (line) radial distribution curve and difference curve (below, multiplied by 2) of $GdCl_3$.

Table 4 Vibrational frequencies of lanthanide trichlorides[a]

Ln	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}	ν_4/cm^{-1}
Gd	(330)	57	326	84
Tm	(345)	61	335	88
Lu	(350)	63	340	90

[a] The ν_2, ν_3, and ν_4 frequencies (except ν_3 for $GdCl_3$) were taken from matrix isolation studies[3,4,14] with appropriate matrix shift corrections. The frequency ν_3 for $GdCl_3$ was taken from a gas-phase spectroscopic experiment.[3] Values given in parentheses were obtained using the experimental l_g(M–X) amplitudes and potential function parameters.

Dynamic model for description of the bending vibration in MX_3 molecules

A dynamic model similar to the model of linear triatomic molecules described by Samdal[13] was applied for description of the nuclear dynamics of planar and quasiplanar MX_3 molecules. The coordinate of the A_2'' vibration (ν_2 frequency) was considered to be non-rigid while all other vibrations were treated in the approach of infinitesimal vibrations. The bending vibration potential $V(a)$ was approximated by a function of k_2, k_4 as well as γ. All GED experimental values [r_g(M–X), r_g(X···X), l(M–X), l(X···X), X–M–X, δ(X···X)] and experimental vibration frequencies (ν_2, ν_3, ν_4) were used to determine the function parameters. The $V(a)$ potential is expressed as in eqn. (1) where a is the instantaneous angle

$$V(a) = k_2R^2(\Delta a)^2 + k_4R^4(\Delta a)^4 + (f_r + f_{rr})[\gamma\Delta r(a)]^2 \quad (1)$$

between the edge and the altitude of the pyramid and $\Delta a = \pi/2 - a$. The potential describes the energy alteration during the change of the valence angle and that owing to the change of internuclear distance $\gamma\Delta r(a)$. The γ value defines the halogen atoms trajectory curvature; $\gamma = 1$ when the trajectory is linear. When the r(M–X) internuclear distance is not altered in the process of vibration, $\gamma = 0$. The probability density function applied for averaging the values depending on the valence angle is given in eqn. (2).

$$P(a) = \exp(-V(a)/kT)/\int \exp(-V(a)/kT)\mathrm{d}a \quad (2)$$

The expressions for instantaneous internuclear distances, valence angle, and dynamic amplitude corrections are given in eqn. (3)–(8).

$$r(a) = r_{min} + \gamma\Delta r(a) \quad (3)$$

$$\Delta r(a) = [r_{min}/\sin(a)] - r_{min} \quad (4)$$

$$R(a) = \sqrt{3}r(a)\cdot\sin(a) \quad (5)$$

$$\sin(\tfrac{1}{2}\mathrm{X–M–X}) = (\sqrt{3}/2)\sin(\alpha) \quad (6)$$

$$l^2_{dyn1} = \int(r(a) - r_{min})^2P(a)\mathrm{d}a \quad (7)$$

$$l^2_{dyn2} = \int(\sqrt{3}r(a)\cdot\sin(a) - \sqrt{3}r_{min})^2P(a)\mathrm{d}a \quad (8)$$

Table 5 Experimental and calculated (by dynamic model and the approach of infinitesimal vibrations) parameters of lanthanide trichlorides[a]

	$GdCl_3$			$TmCl_3$			$LuCl_3$		
	Exp.	Dyn.	Inf.	Exp.	Dyn.	Inf.	Exp.	Dyn.	Inf.
l_g(Ln–Cl)/pm	9.6(1)	9.51	9.45	8.9(2)	9.01	8.96	8.6(2)	8.60	8.60
$l_g(Cl\cdots Cl)$/pm	33.3(12)	33.3	28.3	30.8(18)	31.6	26.5	31.5(11)	31.0	25.7
Cl–Ln–Cl/°	117.0(11)	117.1	116.8	116.2(14)	117.2	117.2	117.9(13)	117.3	117.5
$\delta(Cl\cdots Cl)$/pm	6.5(18)	6.48	7.11	8.2(23)	6.09	5.95	4.4(20)	5.67	5.32
γ		0.087			0.081			0	
k_2		0.0047			0.0061			0.0066	
k_4		0.0089			0.0087			0.0098	

[a] Exp. = experimental data, Dyn. = dynamic model, Inf. = the approach of infinitesimal vibrations.

Results and discussion

In order to determine the equilibrium geometry, calculations of the theoretical shrinkage and amplitudes were implemented for $GdCl_3$, $TmCl_3$, and $LuCl_3$. The vibrational frequencies employed in the approach of infinitesimal vibrations and the dynamic model calculations are shown in Table 4. The experimental information on vibrational frequencies of the lanthanide trichlorides was mainly obtained by two groups of authors, the data having fundamental contradictions. In matrix isolation studies of $LaCl_3$, $GdCl_3$, and $LuCl_3$, Maltsev and coworkers[3,4,14] recorded three bands. The molecules were suggested to be planar or close to that because of the absence of a band which could be assigned to frequency ν_1. Konings and coworkers[15] interpreted a gas-phase spectrum as containing four bands. The bands assigned to the ν_1 and ν_3 frequencies were of almost equal intensity, which could indicate a strongly pyramidal structure. The value of $l_g(Cl\cdots Cl) = 45$ pm calculated using these frequencies is extremely overestimated compared to GED data. Thus, the ν_2 and ν_4 frequencies (and ν_3 for $TmCl_3$ and $LuCl_3$) were taken from the matrix isolation studies[3,4,14] with appropriate matrix shift corrections. For $GdCl_3$ the frequency ν_3 determined by gas-phase spectroscopic experiment[3] was used. The frequency ν_1 is obtained on the basis of the experimental l_g(M–X) amplitudes and potential function parameters.

The values of r.m.s. amplitudes, valence angle and shrinkage calculated by the dynamic model are shown in Table 5, along with the experimental data and the theoretical values calculated by the approach of infinitesimal vibrations. Total calculated amplitudes are obtained by adding the dynamic corrections described above to the values calculated by the approach of infinitesimal vibrations. For all three molecules both the infinitesimal vibrations and the dynamic model approaches yield shrinkage values that are consistent with the experimental values within the uncertainty limit. The positive values of k_2 and k_4 indicate a planar D_{3h} equilibrium structure for $GdCl_3$, $LuCl_3$, and $TmCl_3$ molecules. The infinitesimal vibrations approach gives a value of $l_g(Cl\cdots Cl)$ which is significantly lower than the experimental one for all molecules in question. In the dynamic model, k_2, k_4, and γ values were optimized in order to adjust the calculated amplitudes l_g(Ln–Cl), $l_g(Cl\cdots Cl)$ and shrinkage to the experimental values. For all these molecules the $V(a)$ potential demonstrates more quartic character than quadratic. It is to be noted that the $k_2:k_4$ ratio increases from $GdCl_3$ to $TmCl_3$ and $LuCl_3$ (see Table 5).

In conclusion it has to be emphasized that lanthanide trichlorides are considered to be pyramidal according to the existing experimental data in the literature. The recent series of joint gas-phase electron diffraction and mass spectrometric experiments yielded a planar equilibrium structure for the three trichlorides mentioned above. The r.m.s. amplitudes and shrinkage calculated using a D_{3h} dynamic model are in good agreement with the experimental values. According to the new experimental results reported in this work, and in view of the fact that the most recent calculations also favour planar equilibrium structures, the structures of the remaining lanthanide trichlorides should be reinvestigated.

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