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Structure of monomeric and dimeric molecules of erbium tribromide from gas-phase electron diffraction data

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The structural investigation of molecules in the vapour over erbium tribromide has been performed by synchronous gas-phase electron diffraction and mass spectrometry at $T = 1095(10)$ K. The presence of a small amount (2.5%) of dimeric molecules was detected. For $ErBr_3$ the thermal average bond length r_g(Er–Br) = 258.2(6) pm and the valence angle $\angle_g$(Br–Er–Br) = 116.0(14)° have been determined. This value of the average bond angle corresponds to the planar or near planar equilibrium structure of the monomeric molecule taking into account the shrinkage effect. The structural parameters of Er_2Br_6 have also been obtained.

Introduction

The present gas-phase electron diffraction (GED) study is the first structure investigation of the $ErBr_3$ molecule by an experimental technique. The experimental vibrational spectra of this molecule are also unknown. According to the GED studies carried out in the 1970s (for a summary see the paper of E. Z. Zasorin)[1] the investigated lanthanide trihalides (PrF_3, GdF_3, HoF_3, $LaCl_3$, $PrCl_3$, $GdCl_3$, $TbCl_3$, $HoCl_3$, $LuCl_3$, $LaBr_3$, $GdBr_3$, $LuBr_3$, PrI_3, NdI_3, GdI_3 and LuI_3) were found to be non-planar and of C_{3v} symmetry. In contrast to these results the recent GED reinvestigations of $LuCl_3$[2] and $GdCl_3$[3] and the new investigations of CeI_3,[4] $TmCl_3$[5] and $HoBr_3$[6] have proved that the determined deviations of the thermal-average valence angles Hal–Ln–Hal from 120° may be totally attributed to shrinkage. Moreover the analysis of the experimental data in terms of a dynamic model has shown that gadolinium, thulium and lutetium trichlorides have a planar equilibrium structure with D_{3h} symmetry.[3] In contradiction to this trend the erbium trichloride was found to be pyramidal.[7] This fact makes the investigation of other erbium trihalides especially desirable.

Experimental

A synchronous gas-phase electron diffraction and mass spectrometric experiment was carried out on the modified EMR-100/APDM-1 unit.[8,9] A commercial sample with a purity of 99% was evaporated at 1095(10) K from a molybdenum cell with a cylindrical effusion nozzle of 0.6 × 1.0 mm size (diameter × length). The ratio of the evaporation area to the effusion orifice area was above 500. The vapour composition was monitored by mass spectroscopy during the whole experiment, including the exposition of the photoplates. Mass spectra of the vapour over $ErBr_3$ were recorded at an ionisation voltage of 50 V (see Table 1). It was assumed that the $Er_2Br_5^+$ ion originated from the dimeric molecules, while the other ions arose from the monomer. The ratio of the ionisation cross-sections of Er_2Br_6 and $ErBr_3$ was assumed to be 2 : 1. The dimer concentration calculated on the basis of the mass spectral data was 2.5(10) mol%. No other volatile byproducts were observed.

Table 1 Mass spectral data of the vapour over $ErBr_3$ (nozzle temperature 1095 K, ionizing electron energy 50 eV, % intensities indicated)

Er^+	$ErBr^+$	$ErBr_2^+$	$ErBr_3^+$	$Er_2Br_5^+$	Er^{++}
63.7	32.7	100	22.7	11.2	13.1

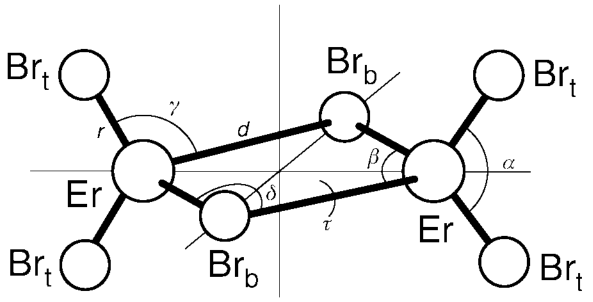

Fig. 1 Molecular model (D_{2h} symmetry) and internal coordinates for Er_2Br_6 (r, d, stretch; α, β, δ and γ, bend; τ, torsion).

Electron diffraction patterns were obtained for the short (L_1 = 338 mm) and long (L_2 = 598 mm) camera distances at an accelerating voltage of 71 kV. The wavelengths of electrons (4.436 and 4.480 pm for L_1 and L_2, respectively) were determined using ZnO powder. The optical densities were measured by a computer controlled MD-100 (Carl Zeiss, Jena) microdensitometer.[10] Five and three plates obtained from the long and short camera distances, respectively, were used in the analysis. A rectangular area of 120 × 8 mm along the diagonal was scanned at each plate.

Structure analysis

A least-squares analysis of the experimental data was performed using a modified version of the KCED program.[11] The final refinement was performed taking into account the

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Table 2 Results of the least-squares analysis[a]

s_{min}–s_{max}/nm^{-1}	18–139	36–242	18–242
Monomer			
r_a(Er–Br)$_{mon}$/pm	257.51(3)	258.00(6)	257.86(5)
r_a(Br···Br)$_{mon}$/pm	435.4(10)	434.7(18)	435.1(9)
l(Er–Br)$_{mon}$/pm	9.60(7)	9.66(4)	9.70(4)
l(Br···Br)$_{mon}$/pm	35.3(5)	35.6(13)	34.9(7)
κ(Er–Br)$_{mon}$/pm^3	20[b]	16(4)	12(4)
Dimer			
r_a(Er···Er)$_{dim}$/pm	411(6)	425(13)	416(8)
r_a(Br$_b$···Br$_b$)$_{dim}$/pm	351(7)	338(17)	355(9)
$\angle_a$(Er···Er–Br$_t$)$_{dim}$/°	120(6)	124(8)	123(7)
Dimer amount/mol%	4.3(20)[c]	3.8(20)[c]	3.0(20)[c]
R_f (%)	1.80	3.53	3.34

[a] σ_{LS} given in parentheses. The following correlation coefficients had values larger than |0.6|: r(Er···Er)$_{dim}$ and r(Br$_b$···Br$_b$)$_{dim}$ = −0.96, r(Er–Br)$_{mon}$ and κ(Er–Br)$_{mon}$ = 0.86, l(Br···Br)$_{mon}$ and ∠(Er···Er–Br$_t$)$_{dim}$ = −0.83, r(Br···Br)$_{mon}$ and r(Er···Er)$_{dim}$ = −0.80, r(Er···Er)$_{dim}$ and l(Br···Br)$_{mon}$ = 0.76, r(Br···Br)$_{mon}$ and r(Br$_b$···Br$_b$)$_{dim}$ = 0.75, l(Br···Br)$_{mon}$ and r(Br$_b$···Br$_b$)$_{dim}$ = −0.72, scale (L_1) and scale (L_2) = 0.62. [b] Fixed, cannot be determined. [c] Estimated error.

presence of both monomeric and dimeric species, as detected by mass spectrometry. It was postulated that the $ErBr_3$ molecule has a threefold symmetry axis. The D_{2h} symmetry model with four Er–Br$_b$ bridging bonds (see Fig. 1) was assumed for the Er_2Br_6 dimer, as it was found for the similar Lu_2Cl_6 molecule.[2] The internuclear distances r_a(Er–Br) and r_a(Br···Br), the root mean square amplitudes l(Er–Br) and l(Br···Br), the asymmetry constant κ(Er–Br) for the monomer and the r_a(Er···Er) and r_a(Br$_b$···Br$_b$) distances and the $\angle_a$(Er···Er–Br$_t$) angle of the dimer were refined as independent parameters. The bond length r_a(Er–Br$_t$) in the dimer was assumed to be equal to r_a(Er–Br) in the monomer. The ratio of the molecular species concentration in the vapour was also refined.

The r_a structure was converted to the geometrically consistent r_α structure taking into account the corrections for perpendicular vibrations. These corrections and shrinkage for the monomer were calculated using formulae by Cyvin[12] from the frequencies ν_1 = 245(10) cm^{-1}, ν_2 = 40(5) cm^{-1}, ν_3 = 245(10) cm^{-1}, ν_4 = 50(5) cm^{-1} estimated using data for similar molecules.[6] The mean amplitudes and the perpendicular vibrational corrections for the dimer were calculated[13] using the estimated force field f_r = 1.77 mdyn Å^{-1}, f_d = 0.95 mdyn Å^{-1}, f_α = 0.45 mdyn Å, f_β = 0.3 mdyn Å, f_γ = 0.405 mdyn Å, f_δ = 0.4 mdyn Å, f_τ = 0.108 mdyn Å. It was proved that the uncertainties of the estimated force constants for the dimer do not bring any noticeable influence on the refined parameters of the monomer. The difference between the r_a(Er–Br) values determined by the refinements with and without vibrational corrections for the dimeric molecule is negligible (less than 0.05 pm).

The results of the least-squares analysis of experimental data are given in Table 2. The experimental and calculated molecular intensity curves $sM(s)$ and their differences are shown in Fig. 2, the corresponding radial distribution curves $f(r)$ are displayed in Fig. 3.

The obtained structural parameters of $ErBr_3$ and Er_2Br_6 are presented in Tables 3 and 4, respectively. The dimer concentration determined by the least-squares refinement is 3(2) mol%, being in good agreement with the mass spectral data (2.5 mol%, see Experimental section).

Results and discussion

Although the amount of dimeric molecules in the vapour at the experimental temperature was small, it seemed to be important to take into account their presence for the precise structural determination. The analysis that neglects the presence of Er_2Br_6 leads to the overestimation of the r(Er–Br) bond length in the monomer by 0.6 pm.

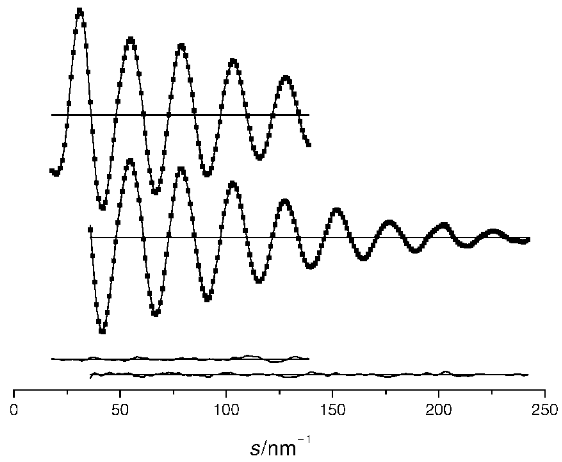

Fig. 2 Experimental (dots) and theoretical (lines) molecular intensity curves and difference curves (below).

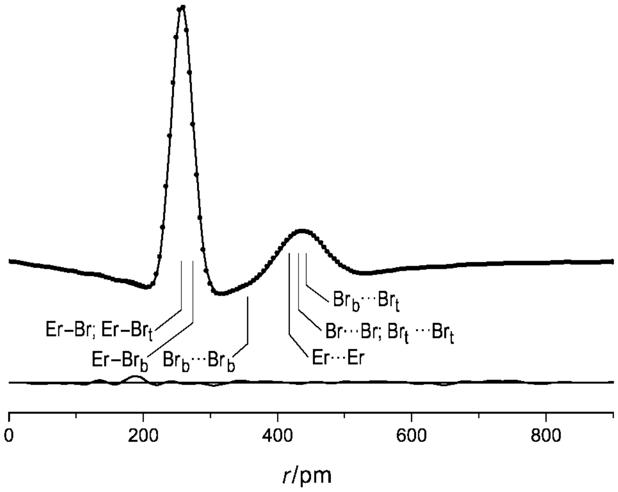

Fig. 3 Experimental (dots) and calculated (line) radial distribution curve and difference curve (below).

The obtained value of r_g(Er–Br) [258.2(6) pm] in $ErBr_3$ is shorter, by 1.3 pm, than r_g(Ho–Br) [259.5(6) pm] in $HoBr_3$[6] and 15.2 pm longer than r_g(Er–Cl) [243.0(5) pm] in $ErCl_3$.[7] Practically the same differences (1 pm and 15 pm, respectively) were obtained by *ab initio* calculations at the multiconfiguration level of theory (MCSCF) using effective core potentials (ECP) for lanthanides and halogens.[14] However it should be noted that the absolute values of the metal–halogen bond lengths r(E–Cl) = 248 pm, r(Ho–Br) = 264 pm, r(Er–Br) = 263 pm in corresponding molecules obtained by quantum-chemical calculations[14] are about 5 pm longer than the experimental r_g ones. The equilibrium bond length r_e(Er–Br) can be roughly estimated by the formula of Bartell,[15] $r_g - r_e = 3al$(Er–Br)^2/2, where a is the Morse constant. According to the data of ref. 16 the a constant can be estimated to be 150(50) pm^{-1}. This approach yields r_e(Er–Br) = 256.1(9) pm which is 7 pm shorter than that from *ab initio* calculations.[14]

The "effective" bond angle $\angle_g$Br–Er–Br was found to be 116.0(14)°. Taking into account the corrections for perpendicular vibrations calculated from the estimated frequencies (see above) the angle $\angle_\alpha$(Br–Er–Br) was obtained as 120(2)° (see Table 3). The estimated total error of the angle also includes an error due to the uncertainties of the vibrational frequencies mentioned above. This result shows that the obtained "effective" deviation from the planar equilibrium configuration could be totally assigned to shrinkage. However, the quasi-planarity or a very small deviation from the planarity cannot be ruled

Table 3 Structural parameters of $ErBr_3$[a]

r_g(Er–Br)/pm	r_g(Br···Br)/pm	$\angle_\alpha$(Br–Er–Br)/°	δ_{exp}(Br···Br)[b]/pm	δ_{calc}(Br···Br)[c]/pm
258.2(6)	437.9(25)	120(2)	9.4(27)	8.8

[a] Estimated total errors σ_{tot} are shown in parentheses; σ_{tot} for r_g distances were calculated using the formula: $\sigma_{tot} = [(2.5\sigma_{LS})^2 + \sigma_{sc}{}^2]^{1/2}$, where σ_{sc} was assumed to be $0.002r_g$; σ_{tot} for the bond angle was calculated from σ_{tot} of the distances also taking into account an error due to the uncertainties of the estimated vibrational frequencies, see text. [b] Experimental shrinkage $\delta_{calc}(Br \cdots Br) = \surd 3 r_g(Er–Br) - r_g(Br \cdots Br)$. [c] Shrinkage calculated for the planar configuration using the estimated frequencies, see text.

Table 4 Structural parameters of Er_2Br_6[a]

r_g(Er–Br$_t$)[b]/pm	r_g(Er–Br$_b$)/pm	$\angle_\alpha$(Br$_t$–Er–Br$_t$)/°	$\angle_\alpha$(Br$_b$–Er–Br$_b$)/°
258.8(6)	275.8(20)	116(7)	81(7)

[a] Estimated total errors shown in parentheses, see footnote *a* in Table 3. [b] r_α(Er–Br) in the monomer and r_α(Er–Br$_t$) were assumed to be equal.

out. The comparison of the thermal average structural parameters of $ErBr_3$ to those of $GdCl_3$,[3] $TmCl_3$,[5] and $LuCl_3$[2] also allows us to suppose that the $ErBr_3$ molecule is planar or nearly planar with a small barrier to inversion. These conclusions agree with the predictions of Molnar and Hargittai[17] based on a simple model taking into account the asphericity of the f-electron shell, the polarizability of the metal ion, and the electronegativity and the size of the halogen ligand.

It is important to find out why the equilibrium molecular structure of $ErCl_3$ was found to be pyramidal,[7] whereas the $ErBr_3$ structure is planar or nearly planar. A possible reason for the different symmetry of these molecules could be the difference in the force of the ligand fields. There are some similar situations for other metal halide molecules when the symmetry of the molecular structure is changed in dependence on the kind of the halogen atoms. For example, WF_4 has nearly D_{4h} symmetry[18] but WCl_4[19] is tetrahedral, and MoF_4[20] has T_d symmetry whereas $MoBr_4$ seems to be of C_{2v} symmetry according to ref. 21. It should be recognised that today it is difficult to ascertain the real reason for the difference in the molecular structure of $ErCl_3$ and $ErBr_3$, and the determination of the electronic states of these molecules, as well as the investigation of the vibrational spectra could contribute to a more precise determination of their molecular conformation.

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