

The Molecular Structure of Monomeric CdCl₂ at 805 K Determined by Gas Electron Diffraction

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Haaland, A., Martinsen, K.-G. and Tremmel, J., 1992. The Molecular Structure of Monomeric CdCl₂ at 805 K Determined by Gas Electron Diffraction. – Acta Chem. Scand. 46: 589–592.

The molecular structures of gaseous main group and transition metal halides have recently been reviewed by M. Hargittai.¹ Several studies have shown that some monomeric Group 2 metal dihalides, CaF₂, SrF₂ and SrCl₂, and the four Ba dihalides are non-linear in the gas phase.¹ The available evidence for Group 12 dihalides, on the other hand, provides little or no evidence for deviation from linearity. Molecular-beam deflection studies indicate that the three fluorides ZnF₂, CdF₂ and HgF₂ and the dichlorides ZnCl₂ and HgCl₂ all are linear.² Careful gas electron diffraction (GED) studies of ZnCl₂, ZnBr₂ and ZnI₂ yield thermal average structures that are non-linear, but corrections for the effect of bending vibrations indicate that the equilibrium conformation is linear.³ The same conclusion is reached in the most recent investigation of CdBr₂,⁴ and an investigation of HgCl₂ found the GED data to be consistent with a linear model.⁵ Data from vibrational spectroscopy are also compatible with linear models.¹

Several years ago we reviewed the structures of main group element chlorides and discussed the variation of element-to-chlorine bond distances across the Periodic Table.⁶ Since then we have wished to determine the structures of the remaining homoleptic chlorides of main group elements which are stable under the experimental conditions of GED, and have published the structures of SeCl₂, TeCl₂ and BiCl₃.^{7–9} M. Hargittai and coworkers have published the structure of monomeric ZnCl₂,³ and in this note we report the structure of monomeric CdCl₂. Girichev and coworkers have determined the structures of monomeric GaCl₃ and InCl₃.^{10,11} We have carried out independent studies of GaCl₃ and InCl₃ and have also determined the molecular structure of PbCl₄. The results of these studies will be reported in the near future.

The low volatility of CdCl₂ required the construction of a radiation-heated nozzle system similar to that described by Tremmel and I. Hargittai.¹² CdCl₂ of stated purity >99% was purchased from Merck-Schuchardt and used without further purification. CdCl₂ is only slightly hygroscopic, and

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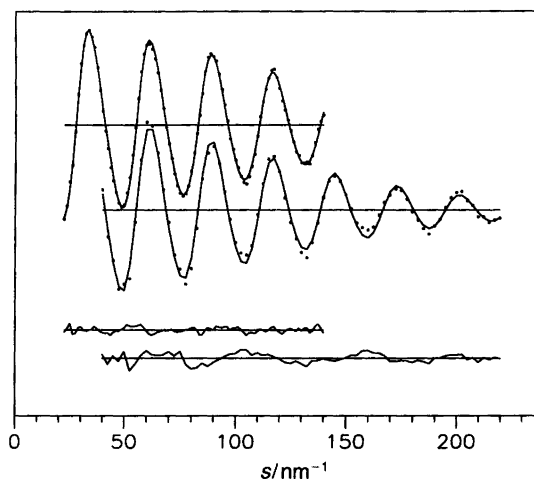


Fig. 1. Calculated (—) and experimental (•) modified molecular intensity curves of CdCl₂ with difference curves below.

is completely dehydrated at pressures less than 1 Torr even at room temperature.¹³ Absorbed water is therefore assumed to be completely eliminated by heating the sample to the temperature required for the recording of GED data under the high vacuum of the electron diffraction unit. The gas electron diffraction data were recorded on a Baltzers Eldigraph KDG-2¹⁴ instrument with sample and nozzle temperatures of 805 ± 15 K, corresponding to a CdCl₂ vapour pressure of about 0.8 Torr.¹⁵ Structure refinements were based on four plates obtained with a nozzle-to-plate distance of 50 cm (s from 22.50 to 150.00 nm⁻¹ with an increment $\Delta s = 1.25$ nm⁻¹) and five plates obtained with a nozzle-to-plate distance of 25 cm (s from 40.00 to 250.00 nm⁻¹ with an increment $\Delta s = 2.50$ nm⁻¹). Optical densities were recorded on the Snoopy densitometer and processed by standard procedures.¹⁶ Atomic scattering factors were taken from Ref. 17. Backgrounds were drawn as eighth degree polynomials to the difference between total and calculated molecular intensities. The resulting modified molecular intensity curves are displayed in Fig. 1.

Table 1. Interatomic distances (r_a), root-mean-square vibrational amplitudes (l) and Cd–Cl asymmetry constant (χ) in CdCl₂ at 805 K obtained by least-squares calculations on the intensity data, with estimated standard deviations in parentheses in units of the last digit.

| | r_a/pm | l/pm | χ/pm^3 |
|--------------------------------------------------------------------------|-----------------|---------------|--------------------|
| Cd–Cl | 228.2(4) | 7.5(3) | 68(20) |
| Cl---Cl | 448.6(16) | 12.2(14) | [0] |
| $\delta = 2r_a(\text{Cd-Cl}) - r_a(\text{Cl---Cl}) = 7.9(16) \text{ pm}$ | | | |
| <i>R</i> -factors | 0.057(50 cm) | 0.131(25 cm) | 0.072(total) |

The length, root-mean-square vibrational amplitude and anharmonicity constant of the Cd–Cl bond, the vibrational amplitude of the non-bonded Cl---Cl distance and the parameter δ , defined by eqn. (1), were refined as inde-

$$\delta = 2r_a(\text{Cd-Cl}) - r_a(\text{Cl---Cl}) \quad (1)$$

pendent parameters along with two scale factors. Only two elements in the correlation matrix were greater than 0.5: the correlation coefficients of $r(\text{Cd-Cl})/\chi(\text{Cd-Cl})$ and $l(\text{Cd-Cl})/\text{SF}(25 \text{ cm})$ were 0.83 and 0.67, respectively. Since the 25 cm data were of poorer quality than the 50 cm data (see *R*-factors in Table 1), they were assigned a relative weight of 0.4. The parameter values obtained are listed in Table 1. Since the least-squares refinement was carried out with a diagonal weight matrix, the e.s.d.s calculated by the program do not include the uncertainty due to data correlation.¹⁸ The estimated standard deviations listed in Table 1 have therefore been multiplied by a factor of two and have also been expanded to include an estimated scale uncertainty of 0.1%.

An experimental radial distribution curve and the counterpart calculated for the best model are shown in Fig. 2.

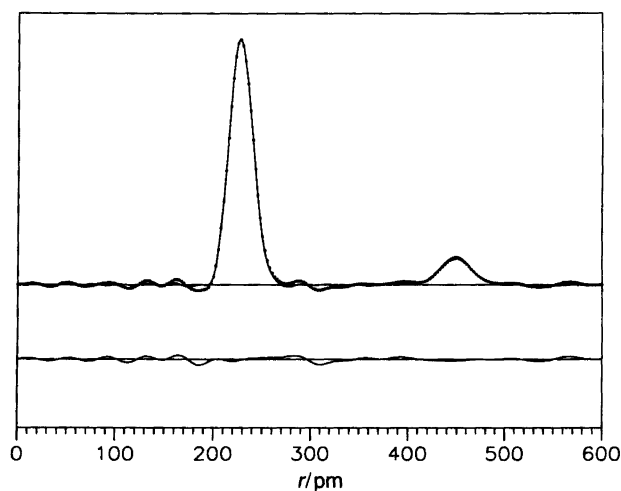


Fig. 2. Experimental (●) and calculated (—) radial distribution curves for monomeric cadmium dichloride at 805 K. Below: Difference curve. Artificial damping constant, $k = 25 \text{ pm}^2$.

Table 2. Normal vibrational modes and force-field of CdCl₂.

| Mode number | Symmetry | ν/cm^{-1} | Force constants /N m ⁻¹ |
|-------------|----------|----------------------|------------------------------------|
| 1 | a_{1g} | 325 ^a | 221 |
| 2 | e_{1u} | 83 ^b | 23 |
| 3 | a_{1u} | 419 ^c | 225 |

^aIn Kr matrix at 20 K.²¹ ^bGas phase.²⁰ ^cIn Kr matrix at 20 K.²²

Since the nozzle system was made from stainless steel, FeCl₂ might be formed under the high-temperature conditions of our experiment. Indeed, mass spectra recorded with the same nozzle at the same temperature contained minor peaks due to FeCl₂⁺ and fragments thereof. Exploratory least-squares calculations in which the amount of FeCl₂ with the known structure (Fe–Cl = 215 pm, $\angle\text{Cl-Fe-Cl} = 180^\circ$)¹⁹ was refined as an impurity, yielded the mole fraction $\chi(\text{FeCl}_2) = 0.04(10)$. We concluded that the amount of FeCl₂ in the molecular beam was insignificant, and in Table 1 we list the parameter values obtained with $\chi(\text{FeCl}_2)$ fixed at 0.00.

It is seen that the thermal average Cl---Cl nonbonded distance is significantly less than twice the thermal average (r_a) Cd–Cl bond distance: $\delta = 7.9(16) \text{ pm}$. The reason for the difference may be that the equilibrium structure of the molecule is non-linear [the observed r_a distances correspond to a thermal average valence angle of $169.3(11)^\circ$] or that the Cl---Cl distance is shortened as an effect of large-amplitude bending vibrations (shrinkage).

The frequency of the bending mode of monomeric CdCl₂ has been determined in the gas phase,²⁰ and the frequencies of the symmetric and asymmetric stretching modes have been determined in krypton matrices.^{21,22} Normal coordinate analysis based on a linear model using the program ASYM²³ yields the symmetry force constants listed in Table 2. The difference between r_a and r_a distances at the temperature of our experiment are calculated to be $D(\text{Cd-Cl}) = r_a(\text{Cd-Cl}) - r_a(\text{Cd-Cl}) = -2.8 \text{ pm}$ and $D(\text{Cl---Cl}) - r_a(\text{Cl---Cl}) = -0.2 \text{ pm}$. Since $r_a(\text{Cl---Cl}) = 2r_a(\text{Cd-Cl})$, it follows that $\delta = D(\text{Cl---Cl}) - 2D(\text{Cd-Cl}) = 5.4 \text{ pm}$, which is in reasonable agreement with the value 7.9(16) pm obtained by the least-squares calculations. We conclude that our GED data are consistent with a linear equilibrium structure.

Table 3. Coordination number of Cd (CN) and Cd–Cl distances in gaseous, molten and crystalline CdCl₂.

| Phase | <i>T</i> /K | CN | <i>R</i> (Cd–Cl)/pm |
|----------------------|-------------|-----|---------------------|
| Gas ^a | 810 | 2 | 228 |
| Melt ^b | 923 | 3.9 | 242 |
| Crystal ^c | Ambient | 6 | 274 |

^aThis work. ^bRef. 25. ^cRef. 26.

Table 4. Bond distances and dissociation energies in the gaseous diatomic radical molecules $^{\bullet}\text{MH}$ and bond distances and mean dissociation energies in gaseous $\text{M}(\text{CH}_3)_2$ and MCl_2 , $\text{M} = \text{Zn}, \text{Cd}, \text{or Hg}$ (all distances in pm and energies in kJ mol^{-1}).

| M | $^{\bullet}\text{M-H}$ | | $\text{M}(\text{CH}_3)_2$ | | MCl_2 | |
|----|------------------------|-----------------|------------------------------------------------|------------------|------------------------|------------------|
| | r_e | D_0 | r_a or r_0 | D | r_a | D_0 |
| Zn | 159.5 ^a | 82 ^a | 193.0(2) ^b 192.9(4) ^c | 186 ^e | 207.2±0.4 ^f | 320 ⁱ |
| Cd | 178.1 ^a | 65 ^a | 211.2(4) ^c | 149 ^e | 228.2 ^g | 281 ⁱ |
| Hg | 177.6 ^a | 26 ^a | 208.3(2) ^d 209.4(5) ^c | 130 ^e | 225.2±0.5 ^h | 225 ⁱ |

^aRef. 24. ^bRef. 27. ^cRef. 28. ^dRef. 29. ^eRef. 30. ^fRef. 3. ^gThis work. ^hRef. 5. ⁱRef. 31.

The vibrational amplitudes calculated from the molecular force field, $l(\text{Cd-Cl}) = 7.2$ pm and $l = 10.2$ pm, are in good agreement with the GED values.

The structure of cadmium dichloride has now been determined in the crystalline phase, where the coordination number of the metal (CN) is six,²⁶ in the melt, where the mean coordination number is 3.9,²⁵ and in the gas phase, where $\text{CN} = 2$. The distances from the Cd atom/ion to the nearest Cl atom/ion in each of the three phases are listed in Table 3, and show the expected increase in bond distance with coordination number.

In Table 4 we list the M-H bond distances and dissociation energies of the diatomic radical molecules $^{\bullet}\text{MH}$, where $\text{M} = \text{Zn}, \text{Cd}$ and Hg , the M-C bond distances and mean M-C mean bond energies in the dimethyl compounds $\text{M}(\text{CH}_3)_2$, and the M-Cl bond distances and mean bond energies in the dichlorides. As is normal for main group elements, the strengths of the M-H, M-C and M-Cl bonds all decrease as Group 12 is descended.

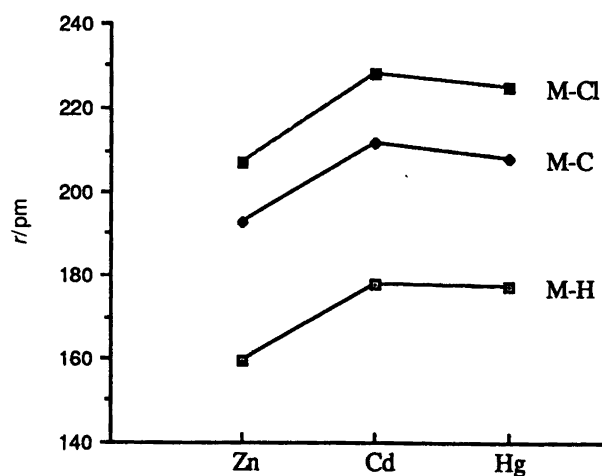


Fig. 3. Bond distances in the radical diatomics $^{\bullet}\text{MH}$ and in gaseous monomeric $\text{M}(\text{CH}_3)_2$ and MCl_2 , $\text{M} = \text{Zn}, \text{Cd}$ or Hg .

The bond distances are displayed in Fig. 3. While the bond distances increase by about 17 pm on going from Zn to Cd, there is a small but statistically significant decrease on going from Cd to Hg. The origin of this anomaly may be a relativistic contraction of the s-orbitals on Hg.³²

Acknowledgements. We are grateful to the Norwegian Research Council for Science and the Humanities (NAVF) for financial support, and to Ing. Hans Vidar Volden and Ing. Snefrid Gundersen for technical assistance.

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Received November 27, 1991.