The Molecular Structure of Different Species of Cuprous Chloride from Gas-Phase Electron Diffraction and Quantum Chemical Calculations

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Abstract: The molecular geometry of gaseous cuprous chloride oligomers was determined by gas-phase electron diffraction at two different temperatures. Quantum chemical calculations were also performed for Cu_nCl_n ($n = 1-4$) molecules. A complex vapor composition was found in both experiments. Molecules of Cu_3Cl_3 and Cu_4Cl_4 were present at the lower temperature (689 K), while dimeric molecules (Cu_2Cl_2) were found in addition to the trimers and tetramers at the higher temperature (1333 K). All Cu_nCl_n species were found to have planar rings by both experiment and computation. The bond lengths from electron diffraction (r_g) at 689 K are 2.166 ± 0.008 Å and 2.141 ± 0.008 Å and the Cu-Cl-Cu bond angles are $73.9 \pm 0.6°$ and $88.0 \pm 0.6°$ for the trimer and the tetramer, respectively. At 1333 K the bond lengths are 2.254 ± 0.011 Å, 2.180 ± 0.011 Å, and 2.155 ± 0.011 Å, and the Cu–Cl–Cu bond angles $67.3 \pm 1.1°$, $74.4 \pm 1.1°$, and $83.6 \pm 1.1°$ for the dimer, trimer, and tetramer, respectively.

Keywords: copper · electron diffraction · halides · molecular structure · quantum chemical calculation

Introduction

Experimental data on the molecular structure of Group 11 halides are scarce. The molecular structures of gold trifluoride and trichloride were recently determined by gas-phase electron diffraction and/or theoretical calculations.[1, 2] These molecules exist as monomers and dimers in the vapor phase, and they all have a somewhat unique structure, different from that of the usual metal halides. The same is true for their crystal structures, especially for gold trifluoride.[3] The gold halides, both monohalides and trihalides, and especially the fluorides[4] and chlorides[5] have been the subject of several computational studies recently, with relatively fewer studies on the bromides[6] and iodides.[6, 7, 8] The cuprous chloride monomer and dimer were studied by coupled-pair functional calculations, including first-order relativistic effects; and an extraordinarily short Cu–Cu distance (2.43 Å) was found in the Cu_2Cl_2 dimer.[9] The metal–metal closed shell interaction was recently studied in cuprous and silver halide dimers.[10] A microwave spectroscopic experiment determined the vibrational and rotational constants and the equilibrium internuclear distance (r_e) of monomeric CuCl.[11] Spectroscopic constants of all Group 11 halides were recently calculated by Stoll and co-workers.[12] There have been earlier attempts to determine the structure of copper(I) chloride by gas-phase electron diffraction (GED) (vide infra). A recent photoelectron spectroscopic study also dealt with the structure of Cu_3Cl_3.[13]

The behavior of the vapor over copper(I) chloride melts was found unusual as long ago as 1879.[14] Vapor pressure measurements suggested that the average molecular mass of the vapor corresponded to a value inconsistent with either the copper(I) chloride monomer or the dimer at any combination of pressure and temperature. Much later an attempt was made to determine the structure of the molecules present in the vapor phase by using GED.[15] Although this study was unsuccessful in producing a clear structure, it was concluded that the results could best be explained by the existence of a trimer with D_{3h} symmetry. Brewer and co-workers[16] estimated the composition of gaseous cuprous chloride as consisting of more than 99.99% trimer and less than 0.001% monomer by measuring thermodynamic properties.

More recent IR[17] and mass spectrometric studies[18, 19] of the vapors of cuprous chloride gave conclusive evidence of the presence of polymeric molecules (up to the pentamer) with the trimer and tetramer being the predominant species under most conditions. Cesaro et al. attempted to determine the symmetry (and force constants) of the trimer and tetramer by using IR spectra and the early GED results of Schomaker and Wang.[15] They concluded that Cu_3Cl_3 has a D_{3h} ring structure,

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while Cu_4Cl_4 is a cube with T_d symmetry. However, to explain the T_d symmetry it was necessary to assume that many of the bands present were not due to the tetramer.

Martin and Schaber also studied the IR spectra of the cuprous chloride vapor and they came to a different conclusion concerning the molecular shape of the tetramer Cu_4Cl_4.[20] Their ionic potential model was in good agreement with the IR spectra only if D_{4h} symmetry was assumed for the tetramer. At the same time, this very model predicted the D_{4h} structure to be 105 $kJ\,mol^{-1}$ less stable than the T_d, but as the authors noted, their potential energy function was rather crude, since it ignored nonionic contributions to the bonding. This is particularly pertinent as it was noted in Schomaker's work that a Cu–Cu interaction was probable on both theoretical and experimental grounds,[15] and it is now known that the "aurophilic"[21] (or generally metallophilic) interaction for the closed shell d^{10} systems is particularly strong. This interaction could be one explanation for the existence of the ring structure in preference to the cube in the tetramer. However, a recent theoretical study showed that cuprophilic interactions are roughly one third as strong as the more common aurophilic interactions, because relativistic effects are smaller in copper compounds.[22]

The GED study of Wang and Schomaker was the first attempt to determine the molecular geometry of cuprous chloride in the vapor phase.[15] The level of sophistication of the early electron diffraction technique and analysis procedure prevented them from giving a definite structure for the molecule, but, supposing that the vapor consisted entirely of trimeric molecules, a bond length and a bond angle were suggested for the D_{3h} symmetry trimer ($r_{CuCl} = 2.160 \pm 0.015$ Å and $\alpha_{CuClCu} \approx 90°$). This structure was then accepted for decades as the structure of cuprous chloride. A new electron diffraction experiment, at different temperatures, was carried out in our Budapest laboratory in 1984. Although the quality of the data was far superior to that of the earlier experiment, the analysis ran into serious difficulties because of the complexity of the vapor composition.

The difficulty with the GED analysis of the cuprous chloride system is caused by several factors. The first is the complicated vapor composition and thus the presence of perhaps several different molecular species in the vapor phase. The second difficulty is caused by the fact that the various bonding and nonbonding distances in these molecules, including the monomer, dimer, trimer, and tetramer, are not very different and thus they cluster close to each other. There is therefore a close correlation among these parameters and they cannot easily be resolved. Furthermore, the polymeric species are characterized by low-frequency, large-amplitude vibrations and, therefore, the so-called shrinkage effect[23] is substantial. This makes the determination of the exact symmetry of the molecules difficult. Hence, information about the molecular structure and symmetry of these species from other sources was essential. High-level quantum chemical calculations have been carried out, partly in order to help the interpretation of the electron diffraction data and partly to get a consistent picture of the structures of the monomeric and different polymeric species of the molecule.

Abstract in Hungarian: *Meghatároztuk a gázállapotú réz(I)-klorid oligomerek molekulaszerkezetét gázfázisú elektrondiffrakcióval két különböző hőmérsékleten. Kvantumkémiai számításokat is végeztünk a* Cu_nCl_n *(*$n = 1-4$*) molekulákra. Mindkét kísérlet során komplex gőzösszetételt találtunk. Az alacsonyabb hőmérsékleten (689 K)* Cu_3Cl_3 *és* Cu_4Cl_4*, a magasabb hőmérsékleten (1333 K) pedig a trimeren és tetrameren kívül dimer,* Cu_2Cl_2*, molekulák alkotják a gőzt. A kísérleti és a számítási eredmények egybehangzóan mutatják, hogy mindhárom* Cu_nCl_n *molekula síkgyűrűs szerkezetű. Az elektrondiffrakciós kötéshosszak 689 K-en: 2.166* $\pm$ *0.008 Å és 2.141* $\pm$ *0.008 Å, a Cu–Cl–Cu kötésszögek: 73.9* $\pm$ *0.6° és 88.0* $\pm$ *0.6° a trimer és a tetramer esetében. 1333 K-en a kötéshosszak: 2.254* $\pm$ *0.011 Å, 2.180* $\pm$ *0.011 Å és 2.155* $\pm$ *0.011 Å, a kötésszögek pedig 67.3* $\pm$ *1.1°, 74.4* $\pm$ *1.1° és 83.6* $\pm$ *1.1° a dimer, a trimer és a tetramer molekulákban.*

Experimental Section

Electron diffraction experiment: Earlier mass spectrometric studies[18, 19] reported that the molar ratio of the different polymeric species varies with temperature. In order to gain as much information as possible about their structure, two experiments were performed at different temperatures. The first selected temperature (689 K) was the lowest possible for the evaporation of the sample. In this experiment a high-temperature nozzle system[24] was used. The nozzle material was stainless steel. At this lower temperature two molecular species of Cu_nCl_n were found in the vapor: about 79 % trimer and 21 % tetramer. The presence of other species, such as chlorine, monomeric CuCl, and the dimer Cu_2Cl_2 was checked during the electron-diffraction structure analysis and could be ruled out. According to the mass spectrometric results[18] in the temperature range of 500–700 K the pentamer content of the vapor is too low to observe its contribution to the total scattering intensity.

A second independent experiment was performed at a significantly higher temperature (1333 K). In this case a double-oven system was used to evaporate the sample.[25] The nozzle material was molybdenum. A different and more complex vapor composition was found during the structure analysis in this experiment. There were three molecular species: about 40 % dimer, 52 % trimer, and 8 % tetramer. The presence of chlorine and the monomer was checked and could be ruled out. Guido et al. reported no pentamer in their mass spectrometric experiment at 900 K.[19]

The details of the experimental conditions are collected in Table 1. The electron scattering factors were taken from the literature.[26] The molecular intensities and radial distributions for both experiments are plotted in Figures 1 and 2. Total experimental intensities for both experiments are available as Supporting Information.

Computational details: The molecular species Cu_nCl_n ($n = 1-4$) were subjected to computation. An initial survey of the possible structural isomers of Cu_2Cl_2, Cu_3Cl_3, and Cu_4Cl_4 was undertaken at the second-order Møller–Plesset level (MP2) with the Los Alamos pseudopotentials and corresponding double-zeta valence basis sets (LANL2DZ), as implemented in Gaussian 98.[27] The small size of the basis set allowed us to consider all possible gas-phase arrangements (with and without symmetry) in a reasonable time frame. The end result of this structural survey allowed us to determine that planar rings (D_{2h}, D_{3h}, and D_{4h} for Cu_2Cl_2, Cu_3Cl_3, and Cu_4Cl_4, respectively) were the favored structures. For Cu_4Cl_4 there is also the possibility of a cubic geometry with T_d symmetry, as indicated earlier by Cesaro et al.[17] and also found for Na_4Cl_4,[28] but our calculations gave this as to be 77 $kJ\,mol^{-1}$ less stable at the MP2/LANL2DZ level. These different molecular arrangements are shown in Figure 3.

The geometries from the above preliminary calculations were then used as the starting points in subsequent geometry optimizations in the second-order Møller–Plesset (MP2) and DFT calculations by using both the BPW91[29] and B3LYP[30] functionals with the aug-CC-PVTZ[31] basis set for

Table 1. Experimental conditions.

nozzle temperature [K]	689		1333	
accelerating voltage [kV]	60		60	
camera ranges [cm]	50	19	50	19
no. of plates[a] used in analysis	5	5	4	4
data intervals [Å^{-1}]	1.875–14.125	9.25–22.75	1.875–14.125	9.00–22.75
data steps [Å^{-1}]	0.125	0.25	0.125	0.25

[a] Kodak electron image plates.

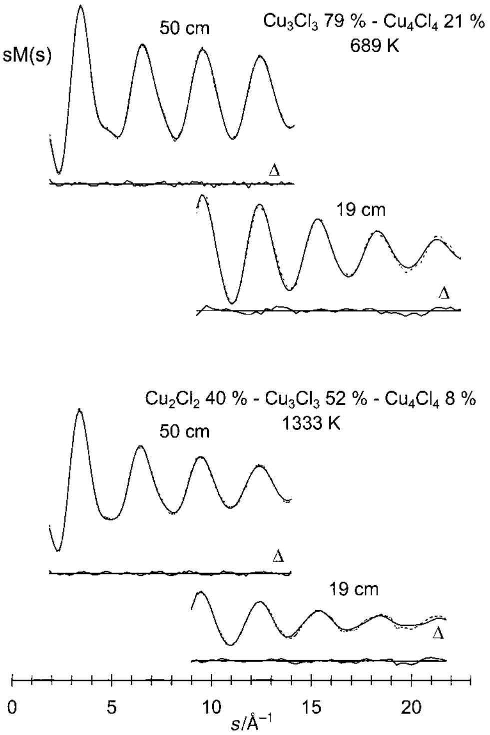

Figure 1. Experimental (dashed line) and calculated (solid line) molecular intensities of the Cu_nCl_n mixture at 689 K (top) and 1333 K (bottom) and their differences (Δ).

Cl and a more accurate Stuttgart pseudopotential[32] and valence basis set[33] combination for Cu. Frequency analyses were carried out on the converged structures. The results of these calculations are presented in Tables 2 and 3. Note that relativistic effects play an important role in the structure of gold halides.[5, 34] Earlier studies showed that this is far less expected for the Cu and Ag halides,[35] since electronegative ligands deplete the 6s occupation on the metal atom and diminish relativistic effects.[34] Nevertheless, scalar relativistic effects are included in the pseudopotentials by adjustment to relativistic atomic data.

Results

Electron diffraction analysis: It was known from previous mass spectrometric[18, 19] and infrared spectroscopic[17, 20] studies that the vapors of cuprous chloride contain several different molecular aggregates. It was evident that without independent structural information from other sources, the GED analysis would not be able to arrive at unambiguous results, as our attempts showed many years ago. The best source for such information is quantum-chemical calculations, performed on the different polymers with the same method and basis set, so that their geometrical parameters can be reliably compared. Useful initial information on molecular symmetry can also be obtained from vibrational spectroscopic studies.

To ascertain that no molecular species possibly present in the vapor was ignored, Cl_2, CuCl, Cu_2Cl_2, Cu_3Cl_3, and Cu_4Cl_4 were included in the analysis. The spectroscopic constants for Cl_2 were taken from the literature.[36] The preliminary refinements strongly suggested that neither chlorine nor monomeric CuCl were present in the vapor in either experiment. For the aggregates, the molecular shape and symmetry was accepted from the computations and spectroscopic measurements: planar ring structures for all of the molecules; D_{2h} symmetry for the dimer, D_{3h} for the trimer, and D_{4h} for the tetramer. Since the tetramer was interpreted with a rocksaltlike, T_d symmetry structure in one of the earlier IR studies,[17] we also tested that possibility in the electron diffraction analysis.

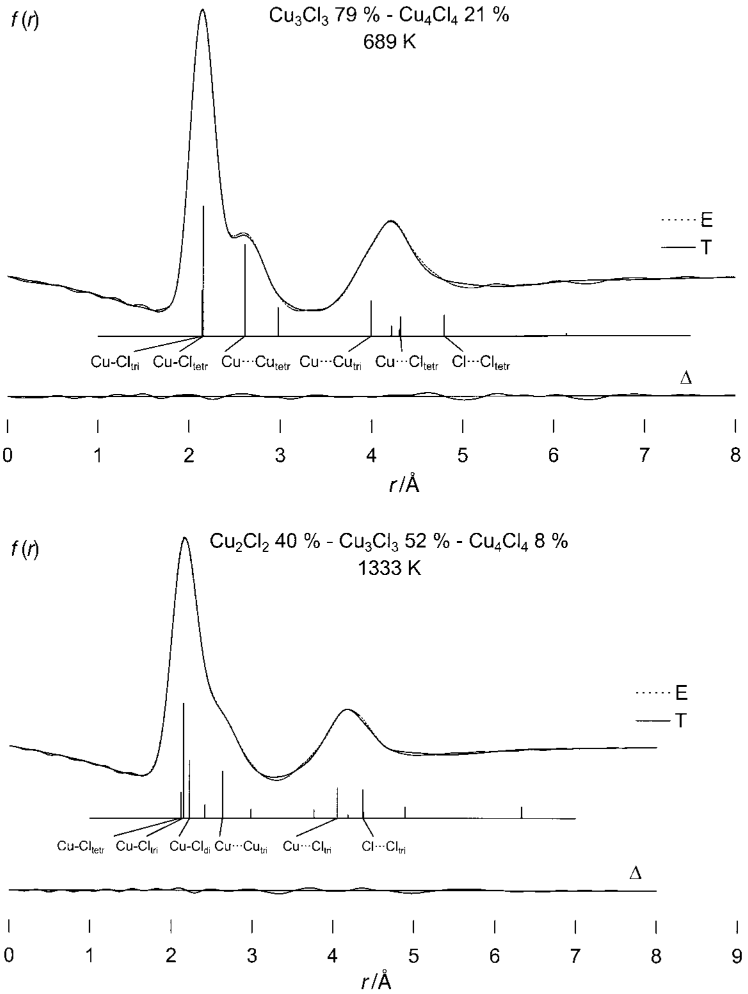

Figure 2. Experimental (E) and calculated (T) radial distributions of the Cu_nCl_n mixture at 689 K (top) and 1333 K (bottom) and their differences (Δ). The vertical bars indicate the relative contribution of different distances.

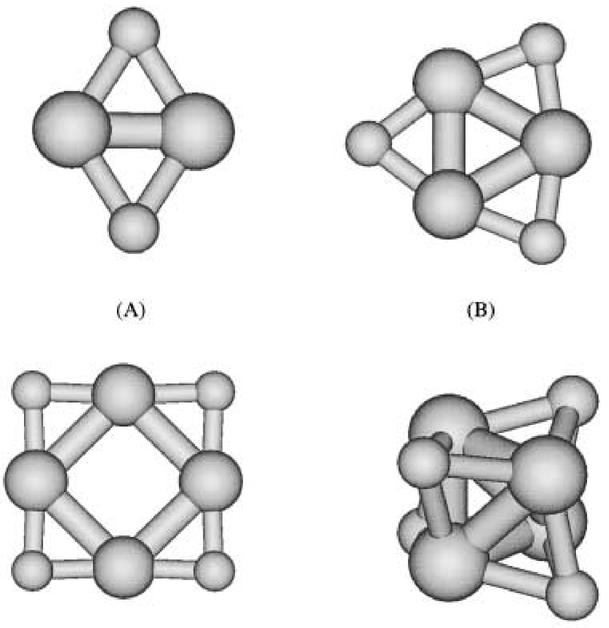

Figure 3. CuCl clusters of A) Cu_2Cl_2 (D_{2h}), B) Cu_3Cl_3 (D_{3h}) and Cu_4Cl_4 in C) D_{4h} and D) T_d symmetry (taken from BPW91 calculations).

Table 2. Computed geometrical parameters and reaction enthalpies of copper chloride clusters.[a]

	Symmetry	BPW91	B3LYP	MP2
r_{MX}				
CuCl	$C_{\infty v}$	2.052	2.070	2.052
Cu_2Cl_2	D_{2h}	2.245	2.260	2.331
Cu_3Cl_3	D_{3h}	2.174	2.183	2.219
Cu_4Cl_4	D_{4h}	2.166	2.157	2.192
	T_d	2.380	2.388	2.429
r_{MM}				
Cu_2Cl_2	D_{2h}	2.311	2.369	2.428
Cu_3Cl_3	D_{3h}	2.525	2.612	2.647
Cu_4Cl_4	D_{4h}	2.841	2.898	2.923
	T_d	3.892	3.905	3.972
α_{MXM}				
Cu_2Cl_2	D_{2h}	62.0	63.2	63.4
Cu_3Cl_3	D_{3h}	71.0	73.5	73.2
Cu_4Cl_4	D_{4h}	82.0	83.6	81.0
	T_d	109.7	109.7	109.7
ΔE				
Cu_2Cl_2	D_{2h}	−188	−180	−193
Cu_3Cl_3	D_{3h}	−512	−477	−497
Cu_4Cl_4	D_{4h}	−706	−669	−705
	T_d	−518	−472	−555
ΔH_0				
Cu_2Cl_2	D_{2h}	−187	−179	−190
Cu_3Cl_3	D_{3h}	−506	−470	−490
Cu_4Cl_4	D_{4h}	−690	−658	−696

[a] Bond lengths r in Å, angles α in degrees, and energy difference ΔE (not corrected for zero-point vibrational effects), and reaction enthalpies ΔH_0 (for the decomposition $n\mathrm{CuCl} \rightarrow (\mathrm{CuCl})_n$) in $\mathrm{kJ\,mol^{-1}}$.

Table 3. Computed (BPW91) and experimental frequencies of the cuprous chloride clusters.[a]

CuCl	$C_{\infty v}$	Σ^+ 418 (14); *415*		
Cu_2Cl_2	D_{2h}	B_{3u} 89 (5.8)	B_{2u} 154 (31); *168*	B_{3g} 186
		A_g 190	B_{1u} 311 (35); *298*	A_g 331
Cu_3Cl_3	D_{3h}	E'' 83	A_2'' 113 (3.6); *116*	E' 121 (2.2); *110*
		A_1' 180	E' 220 (2.1); *234*	A_2' 305
		A_1' 315	E' 390 (30)	
Cu_4Cl_4	D_{4h}	B_{1u} 16	B_{2g} 29.5	B_{2g} 62.6
		A_{1g} 65	B_{2u} 77.0	E_u 82 (2.0)
		E_g 96	A_{2u} 111.9 (4.1)	B_{1g} 252
		E_u 255 (0.3); *248*	A_{1g} 287	A_{2g} 331
		E_u 367 (34); *324*	B_{2g} 381	
	T_d	T_1 33	E 73	T_2 97 (8.4)
		E 137	T_2 145 (20)	A_1 185
		T_2 258 (25)		

[a] Frequencies in $\mathrm{cm^{-1}}$, calculated IR intensities in $\mathrm{km\,mol^{-1}}$ in parentheses. Experimental frequencies are set in italics.

Our computations have shown that the Cu–Cl bond lengths in the different aggregates are similar and thus they cannot likely be resolved in the electron diffraction analysis. Therefore, further constraints had to be introduced. As is well known, the vibrationally averaged experimental geometries and the computed equilibrium geometries differ in their physical meaning; therefore, bond lengths cannot simply be transferred from the computation to the GED analysis.[37] The practice generally followed is to use *differences* of the computed bond lengths rather than the bond lengths themselves as constraints in the GED analysis; this way the differences of physical meaning largely cancel.[38] Another important consideration is the level and accuracy of the computation. However, by using the same method and basis set for all molecular species, the errors caused by their inadequacy can also be expected to cancel to a large extent when we take bond-length differences. We have used this method successfully in previous electron diffraction analyses of metal halide systems.[1, 39]

From among the different computational results, the differences of the B3LYP bond lengths (see Table 2) were used as constraints in the analysis: $\Delta(\mathrm{Cu{-}Cl}) = 0.026$ Å between the trimer and the tetramer and $\Delta(\mathrm{Cu{-}Cl}) = 0.077$ Å between the dimer and the trimer. These values were somewhat different from the BPW91 and MP2 computations, and we have chosen the B3LYP values as the most realistic ones; the dimer–trimer difference seems to be too large from the MP2, while the trimer–tetramer difference too small from the BPW91 computations. The other bond-length differences were also examined in the analysis, but the effects of these changes on the geometrical parameters and the goodness-of-fit were negligible. The estimated consequences of the uncertainties resulting from assuming these differences were taken into account in the calculations of the total errors of the parameters. Starting values of the bond angles were also taken from the B3LYP calculation, but they were then refined in the analysis.

Initial values for the vibrational amplitudes were calculated from the computed frequencies by means of the ASYM20[40] program. Similarly, the so-called perpendicular vibrational amplitudes were calculated in order to take into account the symmetry lowering of the electron diffraction thermal average structure relative to the equilibrium structure. This occurs as a result of the considerable floppyness of the molecules and their low-frequency vibrations. The analysis was performed in terms of the r_a representation, using perpendicular amplitudes from the normal coordinate analysis. The perpendicular amplitudes were included numerically in the program and then removed in the end to give r_g, vibrationally averaged internuclear distances. We also tried to use curvilinear corrections,[41] but it was impossible to reach an acceptable agreement between calculated and experimental intensities by this approach.

The anharmonicity of the vibrations was taken into account by refining the so-called asymmetry parameters of the bond lengths. Their importance was demonstrated by the fact that ignoring them (by assuming the asymmetry parameter to be zero) led to an appreciable increase in the R factor (goodness of fit). Their starting values were estimated by the usual procedure[42] and they were then refined in a group. Similarly, vibrational amplitudes were also refined in groups. The refinement schemes of the two experiments were similar (see Table 4 for details and comments on the refinement). By using the abovementioned constraints and refinement schemes, the bond angles, the majority of the vibrational amplitudes, and the asymmetry parameters of all of the molecules could be refined. Two molecular species, the trimer and the tetramer, were found to be present in the lower temperature experiment, with the trimer prevailing. In the high temperature experiment, the amounts of both the trimer and the tetramer decreased, and about 40% of the vapor content was found to be the dimer. The geometrical parameters of the different molecular forms from both experiments are given in Table 4.

Discussion

Alkali halides are characterized by cluster formation[20, 28, 43, 44] and a comparison with them may be worthwhile. Apparently, there is a definite competition between the ringlike and the cubelike, rocksalt-type structures for most of the alkali halides.[43] For their trimers, just as for Cu_3Cl_3, the ringlike structure is usually favored. For their tetramers and higher polymers, on the other hand, different calculations showed that the relative stability of the ringlike and cubelike structures depends strongly on the level and basis set of the computation (see for example ref. [45]). Besides, the energy difference between the two isomers may be very small, just a few kJ mol^{-1},[46] so that the thermal energy may easily switch the energy levels.

For Cu_4Cl_4 the situation is different. The T_d structure lies 77.8 kJ mol^{-1} above the ring structure at the BPW91 level of theory. Moreover, the IR spectrum of Cesaro et al. contains a peak at 324 cm^{-1}, which does not correspond to any of our computed frequencies for the T_d structure, but agrees better with the IR active E_u mode computed at 367 cm^{-1} for the ring structure. Also, ringlike Cu_nX_n arrangements are well known for a number of coordination compounds of copper.[47] The T_d structure for Cu_4Cl_4 was checked during the GED analysis, but it was ruled out based on the much poorer agreement between experimental and calculated molecular intensities compared with the ringlike structure (twice as large R factor). Thus, much evidence points to the larger stability of the ringlike tetramer of this molecule. At the same time, if phosphine ligands are attached to Cu_4X_4 units (X = Cl, Br: $[\{R_3PCuCl\}_4]$), cubic or ladder-type structures are preferred.[48] A recent X-ray crystallographic study of similar copper(I) chloride complexes also reported "cubanelike" Cu_4Cl_4 units.[49]

It is interesting to speculate on the difference between the structures of CuCl and NaCl. In a purely ionic model the dipole–dipole interactions are maximized in the cubic T_d

Table 4. Geometrical parameters[a] of Cu_2Cl_2, Cu_3Cl_3, and Cu_4Cl_4 from electron diffraction at two different experimental temperatures.

	689 K			1333 K		
	r_g,α	l	κ	r_g,α	l	κ
Cu_2Cl_2						
Cu–Cl				2.254 ± 0.011[b]	0.162 ± 0.012[c]	$7.15 \cdot 10^{-5} \pm 6.8 \times 10^{-5}$[d]
Cu···Cu				2.509 ± 0.013	0.239 ± 0.012[e]	
Cl···Cl				3.725 ± 0.013	0.137[f]	
∢ Cu–Cl–Cu				67.3 ± 1.1		
α%				39.5 ± 1.4		
Cu_3Cl_3						
Cu–Cl	2.166 ± 0.008[b]	0.087 ± 0.007[g]	$5.61 \times 10^{-5} \pm 6.1 \times 10^{-6}$[h]	2.180 ± 0.011[b]	0.146 ± 0.012[c]	$6.34 \times 10^{-5} \pm 6.8 \times 10^{-5}$[d]
Cu···Cu	2.627 ± 0.012	0.178 ± 0.013		2.644 ± 0.012	0.196 ± 0.012[e]	
Cl···Cl	4.331 ± 0.013	0.166 ± 0.014		4.372 ± 0.013	0.182[f]	
∢ Cu–Cl–Cu	73.9 ± 0.6			74.4 ± 1.1		
α%	79.2 ± 0.9			52.2 ± 1.4		
Cu_4Cl_4						
Cu–Cl	2.141 ± 0.008[b]	0.099 ± 0.007[g]	$6.83 \times 10^{-5} \pm 6.1 \times 10^{-6}$[h]	2.155 ± 0.011[b]	0.131 ± 0.012[c]	$7.57 \times 10^{-5} \pm 6.8 \times 10^{-5}$[d]
Cu···Cu	2.997 ± 0.011	0.231 ± 0.014		2.999 ± 0.013	0.190 ± 0.013[e]	
Cl···Cl	4.297 ± 0.011	0.205 ± 0.012		4.372 ± 0.014	0.122[f]	
∢ Cu–Cl–Cu	88.0 ± 0.6			83.6 ± 1.1		
α%	20.8 ± 0.9			8.2 ± 1.4		

[a] Bond lengths (r_g) and vibrational amplitudes (l) in Å, angles (α) in degrees, and asymmetry parameters (κ) in Å^3. Error limits are estimated total errors, including systematic errors and the effect of constraints used in the refinement: $\sigma_t = (2 \times \sigma_{LS}{}^2 + (c \times p)^2 + \Delta^2)^{1/2}$, where σ_{LS} is the standard deviation of the least squares refinement, p is the parameter, c is 0.002 for distances and 0.02 for amplitudes and Δ is the effect of constraints. [b] Differences between dimer, trimer, and tetramer bond lengths were taken from the B3LYP computation and constrained during refinement. [c] Vibrational amplitudes of the dimer, trimer, and tetramer bond lengths refined jointly. [d] Asymmetry parameters of the dimer, trimer, and tetramer bond lengths refined jointly. [e] All Cu···Cu amplitudes refined jointly. [f] Value taken from normal coordinate analysis based on computed frequencies. [g] Vibrational amplitudes of the trimer and tetramer bond lengths refined jointly. [h] Asymmetry parameters of the trimer and tetramer bond lengths refined jointly.

structure. NaCl has a much higher dipole moment (8.97 debye) than our calculated coupled-cluster value for CuCl (5.12 debye at 2.066 Å at the CCSD(T) level), and therefore, prefers the cubic arrangement. On the other hand, CuCl has a strong tendency to form the complex $CuCl_2^-$, which is linear. For the $MCl_2^- \rightarrow MCl + Cl^-$ dissociation we have 220 kJ mol^{-1} for M = Na,[50] and 310 kJ mol^{-1} for M = Cu (calculated from a Born – Haber cycle with data taken from ref. [51]). Hence, the strong tendency of copper toward linear coordination and the less ionic character of CuCl compared to NaCl rationalizes why Cu_4Cl_4 adopts a ringlike structure. This makes CuCl a rather interesting species since the transition from small clusters to the solid state is not immediately evident. CuCl crystallizes in a diamondlike zinc blende structure (ZnS), in which four chlorine atoms surround each copper atom in a tetrahedral arrangement. It would therefore be interesting to investigate Cu_nCl_n clusters with $n > 4$.

Comparing the bond lengths of monomeric CuCl and its dimers, trimers, and tetramers, it is evident that the bond length of the monomer is the shortest, as expected. Considering the larger molecules, the Cu–Cl bond of the dimer is significantly longer (by about 0.2 Å) than that of the monomer. This can be explained by the rather strained structure of the four-membered ring and the repulsion between the chlorine atoms. The Cu–Cu distance, on the other hand, is very short at 2.311 Å (BPW91), and thus might indicate the presence of cuprophilic interaction.[22] However, the atoms-in-molecules (AIM) method of Bader[52] did not reveal such interactions, and the results are more consistent with ionic interactions between the CuCl units.[53] To identify the dispersive type of interactions in such molecules is a nontrivial issue and requires high-level ab initio methods.[22]

For the larger clusters, the bond lengths decrease with the degree of polymerization at all computational levels. This variation can be explained simply by nonbonded interactions; the larger the ring the smaller the repulsion between the chlorine atoms and the shorter the bond length. The same type of bond length variation was observed in the series of different aggregates of LiI.[54] The cubelike T_d structure of the tetramer has the longest Cu–Cl bond length by far with correspondingly short Cu–Cu distances. This structure would be best described as a Cu_4 tetrahedron with each face capped with a Cl atom (see Figure 3D), rather than a bulk structure or a true Cu_4Cl_4 cluster.

Looking at the electron diffraction results, the effect of the increasing experimental temperature causes a slight increase in the trimer and tetramer bond length (0.014 Å in both cases), as would be expected. Comparison of the computed and experimental bond lengths must be done cautiously because of their different physical meaning. Generally speaking, the calculated bond lengths should be shorter than the thermal average experimental values, r_g. Here the BPW91 values are about 0.01 Å longer than the experimental r_g values, but considering the not-too-high level of the computation, this is acceptable. The MP2 bond lengths are much larger than either the DFT or the experimental values for the polymeric species. The calculated bond angles are in good agreement with the experimental ones. The calculated bond length of the monomer, 2.052 Å from both the BPW91 and MP2 computations, is in excellent agreement with the microwave spectroscopic r_e value: 2.051177(8) Å. The B3LYP value of 2.070 Å is worse.

Finally we point out that in order to discuss the gas-phase composition of CuCl clusters at certain pressures and temperatures, precise thermodynamic data of all decomposition reactions have to be known. This is currently a formidable task for computational methods especially for transition-element-containing compounds. Nevertheless, for the Cu_4Cl_4 decomposition into Cu_3Cl_3 and CuCl we obtain $\Delta S = 131$ J mol^{-1} K^{-1} from a thermochemical analysis. Sizable decomposition of Cu_4Cl_4 takes place if the gas-phase equilibrium constant for this reaction is $K = 1$, that is, we obtain $\Delta G/RT = 0$ and the onset of decomposition is approximately $T_d = \Delta H/\Delta S$. Using the data in Table 2 we obtain about $T_d = 1400$ K at one atmosphere pressure, which is roughly in the right range for the experimental conditions.

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