

# Gas-phase structure of nickel dichloride. An electron-diffraction investigation augmented by ab initio and DFT calculations

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## ABSTRACT

The structure of nickel dichloride in the vapor at ca. 1050 K has been studied experimentally by electron diffraction and theoretically by ab initio and DFT molecular orbital calculations. The molecule is found to have a linear equilibrium structure, and from all levels of theory it is predicted to have a triplet ground state. Theory also predicts the existence of a singlet state about 30 kcal/mol less stable than the triplet where the molecule is triangular with a bond angle in the range of about 110 – 117. Two models of the experimental structure were investigated. Model A consisted of 11 “pseudoconformers” distributed at even intervals over the range  $180 \leq \angle(\text{ClNiCl}) \leq 130$  for which the main refined parameter was the distribution (relative weighting) of the pseudoconformers based on an assumed bending potential of the form  $V(\Delta\theta) = V_2(\Delta\theta)^2$ , where  $\Delta\theta$  is the difference of the Cl—Ni—Cl angle from linearity. In this model the pseudoconformational weighting led to averages for the bond- and nonbond distances. Model B was simpler, defined only by values of the bond distance and bond angle. The structural results for Model A are  $\langle r_g(\text{Ni—Cl}) \rangle = 2.067(6)$  Å,  $\langle r_g(\text{Cl}\cdots\text{Cl}) \rangle = 4.037(28)$  Å,  $\langle l_g(\text{Ni—Cl}) \rangle = 0.081(6)$  Å, and  $\langle l_g(\text{Cl}\cdots\text{Cl}) \rangle = 0.136(52)$  Å; in this case the rms amplitudes are for the frame (no contributions from the bending mode). For Model B they are  $\langle r_g(\text{Ni—Cl}) \rangle = 2.059(5)$  Å,  $\langle r_g(\text{Cl}\cdots\text{Cl}) \rangle = 4.041(89)$  Å,  $\langle l_g(\text{Ni—Cl}) \rangle = 0.081(6)$  Å, and  $\langle l_g(\text{Cl}\cdots\text{Cl}) \rangle = 0.159(60)$  Å; the uncertainties are estimated  $2\sigma$ . The theoretical prediction of a linear ground state for nickel dichloride is confirmed by experimental values of about 156 for the bond angle  $\angle(\text{Cl—Ni—Cl})$  in each model, which differs from the theoretical 180 due to the effects of vibrational averaging that arise nearly entirely from the bending mode. The structure is discussed.

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## 1. Introduction

In 1973 we completed a gas-phase electron-diffraction (GED) investigation of the structure of  $\text{NiCl}_2$  at 800C as a part of the thesis work of author L. L. E [1]. From the results it was concluded that the molecule was monomeric with a linear equilibrium structure, but a nonlinear thermal-average structure which doubtless arose from the effects of molecular vibration, particularly the bending mode [2]. Due to the pressure of other work, an account of this study was never published. In 1991 Hargittai et al. [3] reported an extensive GED/vibrational-spectroscopic investigation of structures of the first transition group of metal chlorides and bromides ( $\text{MX}_2$ ; M=Mn, Fe, Co, Ni; X=Cl, Br). It was found that some of the molecules ( $\text{FeCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{FeBr}_2$ ) existed partly as dimers, but the main component of each was overwhelmingly monomeric (89–96%) with a linear equilibrium structure and a nonlinear thermal-average structure.  $\text{NiCl}_2$  was found to be entirely monomeric, consistent with our earlier result.

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Since the time these studies of  $\text{NiCl}_2$  took place, there have been significant advances in both the GED experiment and the analysis of the resulting data. These include the use of auxiliary information from spectroscopic experiments and from quantum mechanical and statistical mechanical theory. However, at the time of our investigation help from the theoretical side was primitive if it existed at all, and in any case could not have been generated because the necessary computational power was lacking. (We presume this was also true of the Hargittai investigation.) Nevertheless, it was possible to investigate the matter of the nonlinear thermal average structure by appropriately designed models. For example, in our study a dynamic model that represented the effects of angle bending on the nonbond distance consisted of a set of “pseudoconformers” comprising molecules with Cl—Ni—Cl angles over a suitable range at fixed intervals, each with a Boltzmann weight determined by a bending potential [4]. With this model, either harmonic or anharmonic motion can be represented through choice of the potential function. (A different approach was used in the Hargittai study; see the original article for details.) In our case the model limitation imposed by the absence of theoretical results amounted to an assumption that the bond length and its associated “frame” vibrational amplitude—the total amplitude minus the contribution from the bending—were invariant with bond angle, i.e., each was the same for all the pseudoconformers. It seemed possible

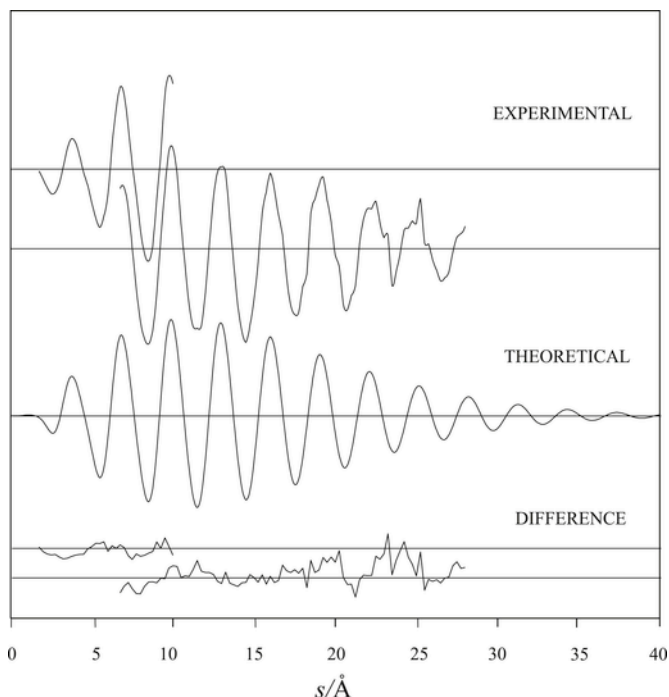


Fig. 1. Intensity curves for  $\text{NiCl}_2$ . The theoretical curve is for model B of Table 1. The difference curves are experimental minus theoretical.

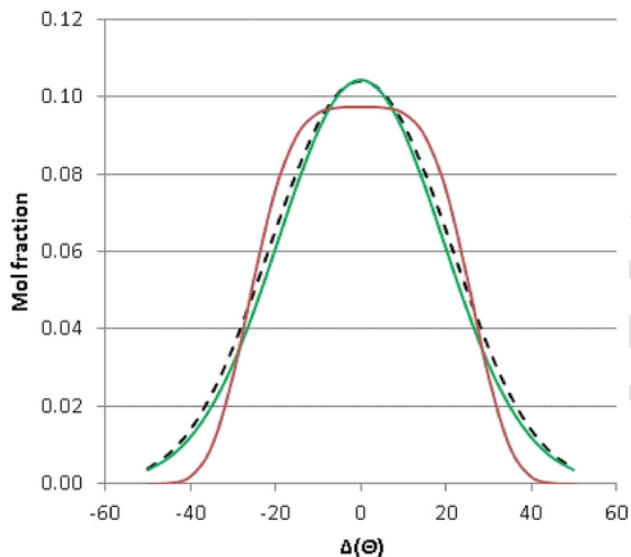


Fig. 2. Distribution of pseudoconformers. The dotted curve is theoretical (from B3LYP/cc-pvtZ), the green and red curves are respectively the best fits from a quadratic and a quartic representation of the bending potential. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

that this and other assumptions implicit in our original model could have had a substantial effect on the parameter values obtained for  $\text{NiCl}_2$ . Accordingly, we decided to re-analyze our old data with use of an upgraded dynamic model that made use of information from *ab initio* and DFT calculations [5]. We also decided to test a much simpler model that hadn't been used in the previous work, one that involved only the two average distances and their associated average rms amplitudes of vibration.

## 2. Experimental

The diffraction data were those obtained for the original work [1] with the Oregon State apparatus operated under the following conditions. Sector,  $r^3$ ; nominal long- and middle camera distances (LC and MC), respectively 75 cm and 30 cm; accelerating voltage, 44 kV; exposure times, 2–3 min (LC) and 5–6 min (MC); nozzle-tip temperature, 1050–1100 K; photographic plates, 8" × 10" Eastman with high contrast "process" emulsion; developer, Kodak D-19 diluted 1 to 1, developing time, 15 min. The sample of anhydrous  $\text{NiCl}_2$  was prepared from reagent grade  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (J. T. Baker) by heating under a stream of dry HCl at about 400 C for 4 h. For the diffraction experiments the product was volatilized in a high-temperature oven constructed of graphite, heated electrically, and supported by a tantalum rod which also served as a conductor. The oven temperature was measured with an optical pyrometer. Water cooling was applied to the end of the assembly furthest from the oven to protect O-ring seals at the vacuum wall; details of the assembly are available in the cited thesis. The oven, a simple version of other ovens used in later high temperature work, lacked radiation shielding to protect the photographic plates from visible light produced at the high oven temperature. To provide this protection the photographic plates were dipped in a solution of Higgins water-soluble black India ink in alcohol [6] which was easily washed off after exposure prior to development.

Three plates from the LC and two from the MC distances were selected for analysis. The procedures used for retrieval of the data and extraction of the molecular scattering have been described [7,8]. The digitized molecular intensity data from each camera distance were averaged to yield two experimental intensity curves (Fig. 1) that were used in refinements of the structure. The data themselves are available as supplementary information.

## 3. Molecular orbital and normal-coordinate calculations

Optimizations of both the singlet and triplet states of the  $\text{NiCl}_2$  structure were carried out over a large range of fixed values for the bond angle at several levels of theory with the Gaussian 09 package [9]. Most of these included DFT/B3LYP and *ab initio*/MP2 with the basis cc-pvtZ, but we also carried out calculations with the bases cc-pvnZ ( $n=q=4$  and  $n=5$ ), and with use of the  $1/n^3$  extrapolation proposed by Puzzarini [10] obtained estimates of  $r_c$  at the complete basis set (CBS) limits.

An important question is whether the multiplicity of the ground state is singlet or triplet. Our calculations support the experimental conclusions of Ashworth et al. [11] that the ground state is a triplet, calculated to be greater than 30 kcal/mol more stable than the singlet. Further, the calculations indicate that the optimized structure of the triplet molecule is linear, but of the singlet molecule it is triangular ( $\angle(\text{Cl}-\text{Ni}-\text{Cl}) \approx 117$  from B3LYP theory and 110 from MP2). With the very strong evidence for a linear structure and a triplet ground state for the molecule, we calculated the energies for different values of the bending angle at 10 intervals over the range 130 - 180 to help assess the form of the bending potential. The dotted curve of Fig. 2 shows the result of the B3LYP/cc-pvtZ optimizations.

## 4. Structure analysis

**Models.** The most important problem in the design of structural models for nickel dichloride is how to take account of the effects of the bending vibration. For this we undertook an analysis of the shape of the theoretical potential in terms of the plausible form  $V(\Delta\theta) = V_2(\Delta\theta)^2 + V_4(\Delta\theta)^4$ . It was found that the theoretical distribution could

**Table 1**  
Experimental and theoretical results ( $r, l/\text{\AA}; \angle/\text{deg}$ ) for  $\text{NiCl}_2^a$ .

|   | experiment                    |                 |           | theory, CBS <sup>b</sup>      |                 |           |           |             |
|---|-------------------------------|-----------------|-----------|-------------------------------|-----------------|-----------|-----------|-------------|
|   | model A <sup>c</sup>          |                 |           | model B (preferred)           |                 |           | B3LYP/MP2 |             |
|   | $r_{\alpha}, \angle_{\alpha}$ | $r_g, \angle_g$ | $l_g$     | $r_{\alpha}, \angle_{\alpha}$ | $r_g, \angle_g$ | $l_g$     | $r_e$     |             |
| $\langle \text{Ni}-\text{Cl} \rangle$           | 2.058(4)                      | 2.067(6)        | 0.081(6)  | 2.056(6)                      | 2.059(5)        | 0.081(6)  | Ni—Cl     | 2.068/2.069 |
| $\langle \text{Cl}-\text{Cl} \rangle$           | 4.029(28)                     | 4.037(28)       | 0.136(52) | 4.033(31)                     | 4.041(89)       | 0.159(60) |           |             |
| $\langle \text{Cl}-\text{Ni}-\text{Cl} \rangle$ | 156.2(46)                     | 156.2(46)       | —         | 156.6(46)                     | 156.6(46)       | —         | Cl—Ni—Cl  | 180.0       |
| $V_2^d$   | $2.48 \times 10^{-3}$         |                 | —         | 0.0                           |                 | —         |           |             |
| $R^e$   | 0.198                         |                 |           | 0.198                         |                 |           |           |             |

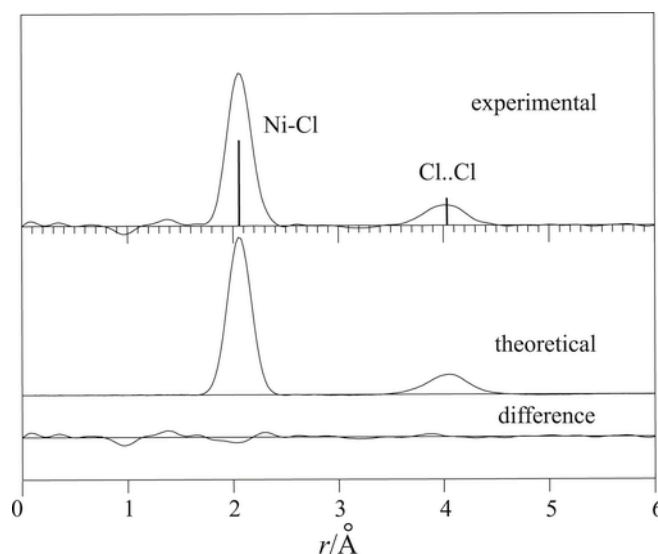
<sup>a</sup> Values of structural parameters are weighted averages. Quantities in parentheses are estimated  $2\sigma$ .

<sup>b</sup> Complete basis set. See ref. 10.

<sup>c</sup> Ranges of variation are 0.013  $\text{\AA}$  for Ni—Cl, zero for  $l_g(\text{Ni}-\text{Cl})$ , 0.010  $\text{\AA}$  for  $l_g(\text{Cl}-\text{Cl})$ .

<sup>d</sup> Coefficient of the assumed bending potential,  $V(\Delta\theta) = V_2(\Delta\theta)^2$ .

<sup>e</sup> Quality-of-fit factor:  $R = (\sum w_i \Delta_i^2 / \sum w_i (s_i I_{m,i}(\text{obsd}))^2)^{1/2}$  where  $\Delta_i = s_i I_{m,i}(\text{obsd}) - s_i I_{m,i}(\text{calc.})$ .



**Fig. 3.** Radial distribution curves from refinement of model B. The relative lengths of the vertical bars are proportional to the weights of the indicated distances. The difference curve is experimental minus theoretical.

**Table 2**  
Correlation matrix x 100 for Model B.

|   | $\sigma_{\text{LS}} \times 100$         | $r(\text{Ni}-\text{Cl})$ | $r(\text{Cl}\cdots\text{Cl})$ | $\angle(\text{Cl}-\text{Ni}-\text{Cl})$ | $l(\text{Ni}-\text{Cl})$ | $l(\text{Cl}\cdots\text{Cl})$ |
|---|---|--------------------------|-------------------------------|---|--------------------------|-------------------------------|
| 1 | $r(\text{Ni}-\text{Cl})$                | 0.15                     | 100                           | 1                                       | -8                       | -8                            |
| 2 | $r(\text{Cl}\cdots\text{Cl})$           | 2.10                     | 1                             | 100                                     | 99                       | 3                             |
| 3 | $\angle(\text{Cl}-\text{Ni}-\text{Cl})$ | 447.                     |                               |   | 100                      | 3                             |
| 4 | $l(\text{Ni}-\text{Cl})$                | 0.19                     |                               |   |                          | 100                           |
| 5 | $l(\text{Cl}\cdots\text{Cl})$           | 15.9                     |                               |   |                          |                               |

be closely matched by a potential that contained only a quadratic term (compare the dotted and green curves in Fig. 2), and thus that the quartic term could be ignored in the design of models for refinement; this was done.

For one of our models, Model A, we chose to use a dynamic representation of the bending mode, which we have done in other cases

including L.L.E.'s thesis work [1]. This model consisted of a set of molecular conformations ("pseudoconformers") distributed along the bending coordinate with Boltzmann weights given by  $w_i = [\exp(-V(\Delta\theta_i)/RT) / \sum_j \exp(-V(\Delta\theta_j)/RT)]$ , where  $\Delta\theta_i$  is the change in the Cl—Ni—Cl angle from linearity. The main parameters for Model A that define the structure thus consisted of the Ni—Cl bond distance in the linear molecule, the potential constant  $V_2$  which determines the weighted distribution of pseudoconformers, and the frame amplitudes of vibration. The structure of a second, much simpler model (B), was defined only by the Ni—Cl distance, the average Cl—Ni—Cl bond angle, and the Ni—Cl and Cl·Cl rms amplitudes of vibration. To have the models representative of the experiments done at 1073 K, we carried out normal coordinate calculations with the program ASYM40 [12,13]. These yielded the quantities required to interconvert the distance types  $r_{\alpha}$ ,  $r_g$ , and  $r_a$  as well as certain relationships among the vibrational amplitudes of the molecular frames.

**Structure refinements.** In an extensive number of tests, it was found that the potential constant  $V_2$  in Model A could not be successfully refined: the  $1\sigma$  uncertainty was larger than the value itself. We adopted a value for  $V_2$ ,  $0.00248 \text{ deg}^{-2}$  that yielded a pseudoconformational distribution very close to that obtained from theory. (Application of this value gave rise to the green curve in Fig. 2.) Refinement of Model B occurred without difficulty. Results for both models are shown in Table 1. Also shown are the CBS  $r_e$  values from theory. Radial distribution curves for Model B are shown in Fig. 3; the curves for Model A are essentially identical. Table 2 contains the correlation matrix for Model B.

## 5. Results and conclusions

There are no indications in our refinement results that suggest one of our two models is the better. We have arbitrarily chosen Model B as our preferred one on the grounds that the more complicated Model A is harder to visualize and in any case has values of the refined parameters that differ insignificantly from those of Model B.

Our experimental results augmented by theoretical calculations strongly support the conclusions of Ashworth et al. [9] that the ground state of gaseous  $\text{NiCl}_2$  is a triplet. All the higher level calculations for a singlet molecule indicated that it is bent ( $\angle \text{Cl}-\text{Ni}-\text{Cl} = 117.4$  from B3LYP/cc-pvtZ and  $110.4$  from MP2/cc-pvtZ) with energies respectively about 37 and 46 kcal/mol greater than for the linear triplet molecules. Although our experimental value for the bond angle in the triplet molecule also differs from linearity, the deviation is relatively small, and unlike the large deviation for the singlet

molecule, is without doubt ascribable to the effects of vibrational averaging of the bending mode.

Our distance values are slightly smaller than those of Hargittai et al. [3] ( $r_g(\text{Ni}-\text{Cl})=2.076$  ( $2\sigma=8$ ) Å and  $r_g(\text{Cl}\cdot\text{Cl})=4.060$  ( $2\sigma=10$ ) Å), but the two sets of values overlap when the listed ranges of uncertainty are taken into account. Hargittai's amplitudes of vibration, ( $l_g(\text{Ni}-\text{Cl})=0.080$  ( $2\sigma=4$ ) Å and  $l_g(\text{Cl}\cdot\text{Cl})=0.134$  ( $2\sigma=12$ ) Å), are in excellent agreement with ours. The large amplitude for the bending mode from both investigations is consistent with the low frequencies of  $73\text{ cm}^{-1}$  and  $77\text{ cm}^{-1}$  we calculate from B3LYP and MP2 levels of theory with the cc-pvtZ basis.

An unusual feature of Table 1 is the value of the "quality of fit factor"  $R$ , equal to 0.20 for both models, which is three or four times larger than is usually obtained. In a perfect experiment the theoretical and experimental intensity curves would be identical and the  $R$  value would be zero, as can be seen from its formula in footnote  $d$  to Table 1, but in a real experiment the data contain random noise which leads to positive values for  $R$ . Since there is no doubt about the structure of  $\text{NiCl}_2$  — two well separated interatomic distances as seen in Fig. 3 — the cause of the large  $R$  value cannot lie in the model type. We believe the cause lies in an exceptionally large amount of random noise in the data, which can be clearly seen in the difference curves of Fig. 1. The reason for the large amount of random noise is probably due to the ink coating of the photographic plates which degraded their response to the scattered electron intensity, as well as a possible uneven removal of the ink coating before development.

A disquieting feature of Table 1 is the comparative values of  $r_g$  and the theoretical  $r_e$  for the Ni—Cl distance, of which the former should be, but is not, the larger. The cause of the discrepancy is uncertain. It could be from the experiment arising from errors in measurements of the electron wavelength or camera distance, or from theory due to uncertainty about the reliability of the CBS values for  $r_e$  which, the reader will recall, were obtained by extrapolation from arbitrary levels of theory and arbitrary basis sets. Further study of this problem seemed fruitless because there is no way to investigate the experimental side, and calculations above the MP2/cc-pv5Z level are too expensive to pursue in further searches for the CBS limit.

Our two models of the nickel dichloride structure provide identical qualities of fit to experiment despite their quite different representations of the consequences of the bending mode. It seems reasonable to assume that each model shows features of the actual structure absent in the other. For example, from the results for Model A the change in the Ni—Cl distance throughout the change of  $50^\circ$  in the bond angle is less than  $0.001$  Å from both the B3LYP and MP2 theoretical levels with the basis cc-pvtZ, which validates the assumption of constancy in this distance adopted in Model B [14]. Further, this near constancy of the bond length reveals something about the form

of the bending. It is curvilinear, i.e., the chlorine atoms move along an arc instead of in a direction perpendicular to the line on which all the atoms lie in the equilibrium structure. On the other hand, Model B provides values for the amplitudes of vibration from all vibrational modes, whereas those from Model A are missing the contribution from the bending mode.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2018.12.100>.

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