the results obtained for II it is likely that the second species is an isomeric form of I analogous to V. Apparently the isomerism is much less favorable for I than for II since no trace of the second isomer of I was observed in solvents other than toluene.

The values of J_2 observed for the proposed isomer V are substantially larger than the values we have previously reported for spin-labeled copper complexes[1,6,14,17] except for those where the nitroxyl-containing ring is attached to a coordinated nitrogen.[1,14] Further studies are underway to elucidate the factors which influence the magnitude of electron–electron coupling in room-temperature solution on EPR spectra.

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Registry No. II, 68212-96-4; III, 68212-97-5; V, 68212-98-6; Cu(batm), 40771-94-6; phenyl isocyanate, 103-71-9; 3-isocyanato-2,2,5,5-tetramethylpyrrolinyl-1-oxy, 68212-42-0.

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Potential Energy Models for Nonbonding and Bonding Interactions in Solid Chlorine

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The observed crystal structure of chlorine at low temperature was used to derive optimized potential energy parameters. Seven potential energy models were tested. The types of energy considered were Buckingham (exp-6) nonbonded, dipolar, quadrupolar, and partial-bonded energy between molecules as represented by a Morse function. The best potential energy model included (exp-6), dipolar, and partial-bond energies. The effective dipole corresponded to point charges of ±0.09 e on the chlorine atoms. The partial-bond energy was about 1–2.7% of the molecular dissociation energy; the best model showed partial bonding which contributed 16% of the total lattice energy.

Introduction

Intermolecular potential energy models for crystalline chlorine have been studied for many years. Yamasaki[1] used a Lennard-Jones (6-12) potential and quadrupole interactions to describe the crystal structure. She determined that a hypothetical cubic structure (space group *Pa*3) has a lower energy than the observed orthorhombic structure (space group *Cmca*). In order to explain the stability of the orthorhombic structure she assumed a partial covalent bond existed between different chlorine molecules. This partial bond corresponded to the observed shortest intermolecular distances of 3.32 Å between chlorine atoms in different molecules. Nyburg[2] showed that a hexagonal structure (space group *Pbm*2) was also predicted by a (6-12) potential model as being more stable than the observed structure. Although the addition of a point quadrupole potential failed to predict the orthorhombic structure, Nyburg found that a finite quadrupole model was successful. The point charges of this quadrupole model were placed at the nuclei and at more than 1.6 Å outside the nuclear positions. The location of effective charges lying so far outside the nuclear positions seemed inherently unreasonable.

Hillier and Rice[3] focused attention on possible partial bonding in the orthorhombic structure by molecular orbital calculations including charge-transfer stabilization. They concluded that charge transfer may contribute about 25% of the cohesive energy but nevertheless failed to predict the observed orthorhombic structure. Nyburg[4] made an extended Hückel molecular orbital calculation on assemblies of chlorine molecules including d-orbital involvement. Although the EHMO energy was only about 5% of the cohesive energy, it was sufficient to stabilize the observed orthorhombic structure. The EHMO energy was found to destabilize the *Pa*3 and $P\bar{6}m2$ structures. English and Venables[5] gave consideration to the possibility of monoclinic space group *C*2/*c*, in addition to the three other space groups mentioned previously. They found that a (6-12) plus point quadrupole potential could not explain the observed structure. They concluded that partial intermolecular bonding stabilizes the observed structure.

Dumas, Vovelle, and Viennot[6] returned to the use of the partial-bond model of Yamasaki, plus (6-12) or (exp-6) nonbonded potentials with no quadrupole potential. They obtained reasonable agreement with the observed lattice vibrational frequencies. However, their potential does not fit the static structure (see the B + M model below). Grout, Leech, and Pawley[7] criticize this work of Dumas et al. on the grounds that a preliminary minimization of the lattice energy was not done. Starr and Williams[8] also determined that such a preliminary minimization was necessary to accurately calculate lattice frequencies.

In this paper we examine the ability of several potential models to predict the lattice constants and molecular tilt in the orthorhombic space group. It transpires that an inter-

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molecular partial bond is necessary for a good fit to the observed structure. Since this partial bond is known to stabilize the orthorhombic structure, no further consideration of the other possible space groups is necessary. We show that none of the previously proposed models, even when optimized, give a good fit to the observed structure (the molecular orbital models were not included). A new dipole model is introduced which leads to an excellent fit to the observed structure. To allow the existence of this dipole, the space group *Cc* for solid chlorine is also considered.

Description of Potential Energy Models

The intramolecular bond is much stronger than the intermolecular forces; to a good approximation we can treat the chlorine molecule as rigid. The bond length of the free molecule[6] is 1.988 Å; in the crystal the observed value[9] is 1.980 Å, essentially unchanged within experimental error. We assume that the potential energy of the crystal is a pairwise sum of isotropic atom–atom terms. The energy contributed by each term for an atom–atom distance r_{ij} is

$$V(r_{ij}) = V_{\mathrm{B}}(r_{ij}) + V_{\mathrm{C}}(r_{ij}) + V_{\mathrm{M}}(r_{ij})$$

In this equation V_{B} is a Buckingham (exp-6) potential consisting of a repulsion and a dispersion part,

$$V_{\mathrm{B}}(r_{ij}) = -Ar_{ij}^{-6} + B\exp(-\alpha r_{ij})$$

V_{C} is a Coulombic potential between point charges q_i and q_j,

$$V_{\mathrm{C}}(r_{ij}) = q_i q_j r_{ij}^{-1}$$

and V_{M} is the Morse potential for the free molecule, multiplied by a constant, p

$$V_{\mathrm{M}}(r_{ij}) = pD\{[1 - \exp(-\beta[r_{ij} - r_{\mathrm{e}}])]^2 - 1\}$$

$r_{ij} < 3.6$ Å; otherwise $V_{\mathrm{M}} = 0$. Thus V_{M} will be applied only to the shortest intermolecular contacts, which are observed as 3.32 Å. The dissociation energy, D, is 239.325 kJ mol^{-1} for the free molecule,[6] and the values for β and r_{e} are known as 2.033 Å^{-1} and 1.988 Å, respectively.

The adjustable parameters in the models are A, B, α, q_i, and p. There is a strong correlation between B and α such that it is difficult to vary both simultaneously. We have selected values for α of 2.50 Å^{-1} (previously used by Dumas[6]) and 3.51 (previously used by Bonadeo[10]) and have optimized B for each case.

The method of optimization of the potential parameters has been described previously.[11] The essential idea is to find by a least-squares fitting procedure the optimum values of the adjustable parameters such that the forces at the observed structure vanish. For the orthorhombic chlorine structure the appropriate forces are F_a, F_b, F_c, and F_θ. The first three are the negative of the first derivatives of the potential energy of the crystal with respect to the lattice constants. F_θ is the negative derivative of the potential energy of the crystal with respect to rotation in the *bc* plane, as required by the space group symmetry. We set up a residual function, R, and minimize it:

$$R(A,B,q,p) = \sum_{i=a,b,c,\theta} w_i F_i^2 + w'(V_{\mathrm{crystal}} - V^0_{\mathrm{crystal}})^2$$

The standard technique of a Taylor's series expansion about a trial model for the potential parameters is used. The last term normalizes the calculated lattice energy to the observed lattice energy, V^0_{crystal}. The weight w' is taken sufficiently large to get the desired agreement. It should be noted that this is a side condition and no merit for the potential parameters is indicated by an agreement of the observed and calculated lattice energy. The observed lattice energy[12] is taken as -31.92 kJ mol^{-1} after correction for the zero-point energy[1] of 1.87 kJ mol^{-1}. The weights w_i were set equal to

$$[\sigma(i)]^{-2}[\partial^2 V_{\mathrm{crystal}}/\partial i^2]^{-2}$$

where the $\sigma(i)$ were estimated as 1% for the lattice constants and 0.02 rad for the molecular tilt.

The observed crystal structure parameters and atomic coordinates were taken from a refinement carried out by Donohue and Goodman.[9] The space group is *Cmca*, with four chlorine molecules in a cell of dimensions $a = 6.24$, $b = 4.48$, and $c = 8.26$ Å. The chlorine atom is located at $y = 0.1161$ and $z = 0.1014$. The molecular centers form a face-centered orthorhombic lattice. The Cl–Cl bond length is 1.980 Å and the tilt of the molecules with respect to c is 31.84°.

The two short distances of 3.32 Å are in the *bc* plane. The next shortest distances are two at 3.74 Å between *bc* layers, two at 3.82 Å within the layer, and four at 3.84 Å between layers. The crystal structure and shortest intermolecular distances are shown in Figure 1.

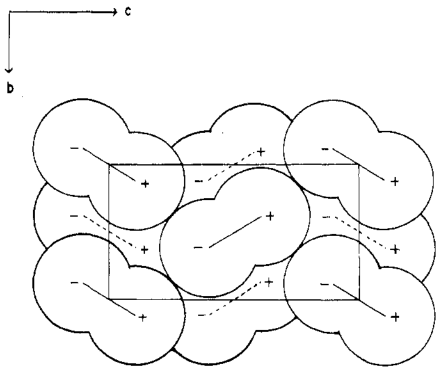

Figure 1. Crystal structure of chlorine, showing the orientation of the molecular dipoles.

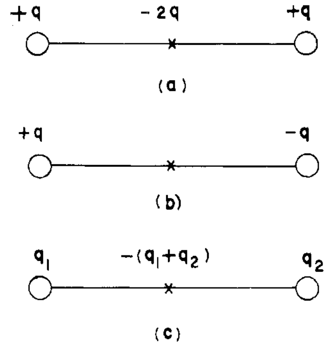

Figure 2. Location of the net atomic charges: (a) finite quadrupole, (b) finite dipole, (c) quadrupole plus dipole model.

The lattice sum was treated by a convergence acceleration technique[13] using a summation limit of 12 Å. It is necessary to use convergence acceleration to achieve accuracy in the evaluation of V_{B} and V_{C}, particularly the latter. We estimate that our lattice sums are converged within 0.1%. Both the first and second derivations of V_{crystal} were evaluated analytically rather than numerically.

Potential Models

We considered seven different potential models, evaluating each model with two values of α. These models are described as follows, with an abbreviation being given for each model.

(1) Buckingham potential only, model B. The adjustable parameters are A and B.

(2) B plus a quadrupole potential, model B + Q. The quadrupole consisted of a net charge $+q$ at each chlorine and a net charge $-2q$ at the bond center. See Figure 2(a). The

Table I. Optimized Potential Parameters Based on Seven Different Potential Models with α Equal to 2.50 or 3.51 (Units Are kJ mol^{-1} and A)

model	α	*R*	*A*	*B*	*q*	*p*
B	2.50	88.705	13 823	43 732	0.000	0.000
	3.51	239.22	9 190	800 680	0.000	0.000
B + Q	2.50		failed to converge			
	3.51		failed to converge			
B + D	2.50	110.308	6 923	24 445	0.373	0.000
	3.51	7.659	3 296	392 829	0.420	0.000
B + Q + D	2.50		failed to converge			
	3.51		failed to converge			
B + M	2.50	0.120	13 557	46 744	0.000	0.090
	3.51	0.030	7 770	931 563	0.000	0.220
B + Q + M	2.50	0.023	13 521	46 706	0.0815	0.092
	3.51	0.009	7 742	929 653	0.0724	0.229
B + D + M	2.50	0.004	13 197	45 572	0.0914	0.083
	3.51	0.003	7 571	909 179	0.0868	0.214

Table II. Deviation of the Calculated Structure Models from the Observed Structure (Units Are A and deg)

	model	α	Δ*a*	Δ*b*	Δ*c*	Δθ
	B	2.50	−0.12	−0.73	1.56	28.8
		3.51	−0.17	−0.79	1.53	18.3
	B + D	2.50	−0.11	0.18	−0.80	12.8
		3.51	−0.16	0.25	−0.79	14.7
	B + M	2.50	0.08	−0.56	1.05	21.3
		3.51	0.09	−0.54	0.92	15.8
	B + Q + M	2.50	0.07	−0.42	0.74	12.1
		3.51	0.08	−0.47	0.79	12.5
	B + D + M	2.50	0.01	−0.05	0.08	1.1
		3.51	0.07	−0.36	0.60	9.0
obsd values			6.24	4.48	8.26	0.0

adjustable parameters are *A*, *B*, and *q*.

(3) *B* plus a dipole potential, model B + D. The dipole consisted of net point charges of $+q$ and $-q$ at each chlorine atom [Figure 2(b)]. To allow this asymmetry the space group becomes *Cc* (monoclinic) locally, as far as the net charges are concerned. The adjustable parameters are *A*, *B*, and *q*.

(4) B plus quadrupole plus dipole potential, model B + Q + D. See Figure 2(c) for the location of the net point charges. The adjustable parameters are *A*, *B*, q_1, and q_2.

(5) B plus Morse potential, model B + M. The adjustable parameters are *A*, *B*, and *p*.

(6) B plus quadrupole plus Morse potential, model B + Q + M. The adjustable parameters are *A*, *B*, *q*, and *p*.

(7) B plus dipole plus Morse potential, model B + D + M. The adjustable parameters are *A*, *B*, *q*, and *p*.

Table I shows the optimized values for the potential parameters, for the two values of α. Model B + Q and B + Q + D seem unreasonable since no converged values for the potential parameters could be found. This behavior indicates that the mathematical form of the potentials cannot describe the stable observed structure.

The weighted forces were minimized (in magnitude) during the calculation of the optimum potential parameters. A further test of the models is to find the calculated structure for which all forces are zero, i.e., to minimize the calculated lattice energy as a function of the structural parameters *a*, *b*, *c*, and θ. This was carried out using a modified version of the molecular packing analysis computer program[14] PCK6. The results of the lattice energy minimization for the various models are shown in Table II. In general, the large calculated deviations in the table correspond to large net forces at the observed structure.

We have also tested the B + M potential parameters of Dumas, Vovelle, and Viennot.[6] For this potential the eigenvalues of the Hessian matrix are not all positive. This means that the model does not have a minimum lattice energy in the vicinity of the observed structure. The calculated forces at the observed structure are generally much larger than those obtained with our model B + M, which does have a positive definite Hessian. We discontinued the lattice energy minimization using the Dumas et al. parameters after large shifts in the structural parameters were obtained with the final minimum not yet in sight. We consider that these potential parameters are not correct, and therefore the calculated lattice frequencies based on them are also in doubt.

Discussion

The previous studies on the chlorine crystal structure strongly indicated that a partial bond is present between the molecules, corresponding to the unusually short distances of 3.32 Å. Our model B + M quantifies this concept. Table II shows that this model still deviates substantially from the observed structure. With $\alpha = 2.5$, *c* is calculated 1.05 Å too large and θ is off by 21.3°. With $\alpha = 3.51$, *c* is calculated 0.92 Å too large and θ is wrong by 15.8°. Table II shows that the B + D model is slightly better than the B + M model.

The dipole model is prohibited by the centrosymmetric orthorhombic space group *Cmca*; the molecules are located on twofolds along the *x* direction. In the corresponding noncentrosymmetric space group, *C*2*ca*, these twofolds are still present. It is necessary to go to the monoclinic space group *Cc* to remove these twofolds and allow the dipole model. The B + D model has an unreasonably large dipole, with *q* equal to 0.373 or 0.420. The addition of a Morse potential greatly decreases *q*; we think that the B + D model should be rejected even though it gives a slightly better agreement than the B + M model. The B + D + M model has only a small value of *q*, so that the departure from orthorhombic symmetry is slight. Possibly this deviation would not be noticed experimentally. Also, the monoclinic domains could be twinned so as to yield averaged orthorhombic symmetry.

A molecular quadrupole is permitted in space group *Cmca*. Although the B + Q model failed, Table II shows that the B + Q + M model was more successful than the B + M model. The magnitude of the quadrupole moment is in a reasonable range, with *q* equal to 0.0815 or 0.0724. However, the fit to the *c* lattice constant and to the molecular tilt is not good; with $\alpha = 2.50$, *c* is off by 0.74 and θ is off by 12.1°.

The B + D + M model shows further improvement of fit. With $\alpha = 2.50$, the fit becomes very good. In the presence of the Morse potential the value of $q = 0.0914$ is much less than the value of $q = 0.373$ in the B + D model. We regard the lower value of *q* as more reasonable on physical grounds. The B + D + M model with $\alpha = 2.50$ is the best model tested by a considerable margin.

The contribution of the partial bond through the Morse potential depends on the value of α. This can easily be understood by noting that we could substitute for the Morse potential a force constant for the 3.32 Å partial bond. Since we have assumed a normal exponential repulsion between these atoms, the force constant must be sufficiently large to overcome this repulsion. With $\alpha = 3.51$, the repulsion potential has a steeper slope which must be balanced by the force constant corresponding to the Morse potential. Therefore *p* is larger when $\alpha = 3.51$. The choice of the isolated molecule Morse potential can be regarded as arbitrary.

The energy contributions of various types are shown in Table III. The larger value of α yields a smaller repulsion energy and a corresponding decrease in the magnitude of the dispersion energy. As noted above, the Coulombic energy of the B + D model seems unreasonably large. The partial bonds contribute about 16% of the total lattice energy if $\alpha = 2.50$ and about 40% of the lattice energy if $\alpha = 3.51$. A different choice of functional form for the partial-bond potential would lead to still different percentages. The *p* values themselves show partial bonds of 8–21%. An alternative view, which we prefer, is to divide the partial-bond energy by the bond energy

Table III. Classification of Energy Types for the Calculated Structure Models[a]

model	α	repulsion	dispersion	Coulombic	Morse
B	2.50	55.4	−88.3	0.0	0.0
	3.51	28.8	−63.1	0.0	0.0
B + D	2.50	38.1	−49.9	−21.4	0.0
	3.51	15.9	−23.3	−26.8	0.0
B + M	2.50	55.7	−82.6	0.0	−5.3
	3.51	28.7	−47.8	0.0	−13.1
B + Q + M	2.50	56.1	−82.6	0.1	−5.6
	3.51	28.7	−47.7	0.1	−13.2
B + D + M	2.50	54.8	−80.4	−1.1	−5.2
	3.51	28.1	−46.3	−0.9	−12.9

[a] The total observed energy is −31.92 kJ mol^{-1}.

of the isolated chlorine molecule. If this description is used, each partial-bond energy ranges from 1.1 to 2.7% of the dissociation energy of chlorine, for the various models considered. The best B + D + M model has a partial-bond energy of 1.1%. The net charge of 0.0914 e on chlorine might be related to the partial bond formation.

We have explored the vicinity of the minimum energy of the B + D + M model. We took grid points at ±0.1 and ±0.2 Å in the lattice constants and ±1 and ±2° in the molecular tilt from the values at the minimum-energy position. The resulting 625 energy values were plotted. Table IV (supplementary material) gives the energy values for the six sections passing through the minimum: *ab*, *ac*, *aθ*, *bc*, *bθ*, and *cθ*. The energy shows the expected positive definite curvature in all sections. The contours are fairly circular and the minimum-energy position is well defined.

If a Cl–Cl dipole exists in the crystal, the infrared spectrum should show a nonzero intensity for the stretching frequency. Walmsley and Anderson[15] observed such infrared stretching frequencies in solid bromine and iodine. Wong and Whalley[16] state that the Cl_2 stretching frequency is absent from the infrared spectrum of solid Cl_2. But they mention experimental problems of high background in the expected frequency region. They also noticed differences in the spectrum which depended on the temperature of deposition of the sample. We think that careful remeasurement of the infrared spectrum of the solid is needed. It is known from the Raman spectrum that the stretching frequency is shifted from 557 cm^{-1} in the gas to 538 cm^{-1} in the crystal at 77 K. While this shift is not as large as those shown by Br_2 or I_2, it indicates a significant interaction which could be accompanied by charge transfer, in agreement with our model. A solution of Cl_2 in benzene,[17] for instance, shows a Cl–Cl infrared stretching absorption at 526 cm^{-1}. Gaseous chlorine dimer, $(Cl_2)_2$, has a detectable observed dipole moment[18] of at least 0.2 D.

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Registry No. chlorine, 7782-50-5.

Supplementary Material Available: Table IV, giving the energy values for the six sections passing through the minimum (1 page). Ordering information is given on any current masthead page.

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Volumes of Activation for Substitution Reactions of Tris(1,10-phenanthroline)- and Tris(2,2′-bipyridyl)iron(II) Complexes with Hydroxide and Cyanide Ions from High-Pressure Solution Kinetics

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The effect of high pressure on the rates of substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ (phen = 1,10-phenanthroline; bpy = 2,2′-bipyridyl) with hydroxide and cyanide ion has been evaluated. All reaction rates are significantly retarded upon the application of pressure. The hydroxide-dependent component of the rate expression exhibits volumes of activation ($\Delta V^{\ddagger}$) of +19.7 ± 0.3 and +21.5 ± 0.4 cm^3 mol^{-1} for substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$, respectively. The cyanide-dependent term exhibits $\Delta V^{\ddagger}$ of +19.8 ± 1.0 and +20.9 ± 1.6 cm^3 mol^{-1} for substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$, respectively. A rate-determining dissociative interchange mechanism is most consistent with the observation that $\Delta V^{\ddagger}$ for substitution of each complex is positive, pressure-independent, and independent of nucleophile.

Introduction

Substitution reactions of diimine metal complexes of the type $M(aa)_3^{n+}$ (aa = phen = 1,10-phenanthroline or aa = bpy = 2,2′-bipyridyl) have been the subject of many investigations which have been reviewed on several occasions previously.[1-4] For the extensively studied $Fe(aa)_3^{2+}$ complexes, the rate of ligand substitution has been observed to be enhanced in the presence of hydroxide, cyanide, and azide ions. A general rate expression of the type

$$k_{obsd} = k_a + k_X[X^-] \qquad (1)$$

has been reported for $X^- = CN^-$ or N_3^- when $[X^-] < 1.0$ M. This expression is also adequate for $X^- = OH^-$ at $[OH^-] \leq 0.1$ M at least, although a further term in $[OH^-]^2$ is necessary

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