are of interest in terms of modifying redox behavior of metalloporphyrins by selective axial ligation. Spectroscopic and electrochemical studies are now in progress to determine if similar effects are obtained for other complexes of metalloporphyrins having closed d shells.

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Registry No. (TPP)Mg(**1**)$_2$, 80186-45-4; (TPP)Mg(**2**)$_2$, 80186-46-5; (TPP)Mg(**3**)$_2$, 80186-47-6; (TPP)Mg(**4**)$_2$, 80206-17-3; (TPP)Mg(**5**)$_2$, 80186-48-7; (TPP)Mg(**6**)$_2$, 80186-49-8; (TPP)Mg(**7**)$_2$, 80186-50-1; (TPP)Mg(**8**)$_2$, 15672-67-0; (TPP)Mg(**9**)$_2$, 80186-51-2; (TPP)Mg(**10**)$_2$, 80186-52-3; (TPP)Mg(**11**)$_2$, 80186-53-4; (TPP)-Mg(**12**)$_2$, 80186-54-5; (TPP)Mg(**13**)$_2$, 80186-55-6; (TPP)Mg(**14**)$_2$, 80186-56-7; (TPP)Mg(**15**)$_2$, 80186-57-8; (TPP)Mg(**16**)$_2$, 80186-58-9; (TPP)Mg(**17**)$_2$, 80186-59-0; (TPP)Mg(**18**)$_2$, 80186-60-3.

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Molecular Structure and Quadratic Force Field of Chromyl Chloride, CrO_2Cl_2

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The molecular structure of chromyl chloride has been reinvestigated at room temperature by gas-phase electron diffraction. The analysis included corrections for the effects of vibrational averaging (shrinkage) calculated from an existing quadratic force field modified slightly by use of our structure to formulate the **G** matrix. Values for the symmetrized force constants are given. The structure results, which are based on and are consistent with C_{2v} symmetry for the molecule, are $r_g(\mathrm{Cr{=}O}) = 1.581\ (2)$ Å, $r_g(\mathrm{Cr{-}Cl}) = 2.126\ (2)$ Å, $r_g(\mathrm{O{\cdots}O}) = 2.564\ (8)$ Å, $r_g(\mathrm{O{\cdots}Cl}) = 3.026\ (4)$ Å, $r_g(\mathrm{Cl{\cdots}Cl}) = 3.547\ (7)$ Å, $\angle_\alpha\mathrm{OCrO} = 108.5\ (4)°$, $\angle_\alpha\mathrm{ClCrCl} = 113.3\ (3)°$, $\angle_\alpha\mathrm{OCrCl} = 108.7\ (1)°$, $l(\mathrm{Cr{=}O}) = 0.047\ (2)$ Å, $l(\mathrm{Cr{-}Cl}) = 0.053\ (2)$ Å, $l(\mathrm{O{\cdots}O}) = 0.070\ (8)$ Å, $l(\mathrm{O{\cdots}Cl}) = 0.091\ (4)$ Å, and $l(\mathrm{Cl{\cdots}Cl}) = 0.105\ (7)$ Å; parenthesized values are estimated 2σ. The calculated shrinkage corrections were tested. It was found that magnitudes about half those calculated gave slightly, but probably not significantly, better agreement with experiment.

Introduction

Valence-shell electron-pair repulsion (VSEPR) theory[2] has been widely used to predict and rationalize the structures of molecules and complex ions. The theory has enjoyed a particularly high degree of success when applied to compounds of the main-group elements, but it is somewhat less successful with compounds of the transition elements. For example, the structure of $TiCl_4$[3] is found to be tetrahedral in accordance with prediction, but $Nb(NMe_2)_5$[4] and WOF_4[5] are both square pyramidal instead of trigonal bipyramidal.

The metal atoms in these compounds are formally in the same oxidation state and have electron configuration d^0. Two other such compounds are the chromyl halides CrO_2F_2 and CrO_2Cl_2, the structures of which also do not agree with prediction from VSEPR theory. Thus both a recent electron-diffraction investigation[6] of CrO_2F_2 and an analysis[7] of its vibrational spectrum assigned a smaller value to the OCrO bond angle than to the FCrF angle, in contradiction to the VSEPR postulate that double bonds occupy more space on the coordination sphere than do single bonds. (An interpretation of the microwave spectrum[8] is in disagreement with this assignment, however.) Similarly, an early electron-diffraction study[9] of CrO_2Cl_2 revealed the OCrO angle to be smaller than the ClCrCl angle, but not by so much as in the fluorine compound.

The present study of chromyl chloride was stimulated by our desire to verify the above puzzling and unexpected result for the relative angle sizes. We also expected to improve the accuracy of the distance and angle measurements from the old study and to obtain values for the vibrational amplitudes.

Experimental Section

A commercial sample (Allied Chemical) of CrO_2Cl_2 was redistilled prior to use and a middle cut taken which was subsequently protected from daylight.

The diffraction experiments were performed in the OSU apparatus with the nozzle tip at room temperature and a sample-bath temperature of 2–5 °C. Other experimental conditions included an r^3 sector, 8 × 10 in. Kodak projector slide plates (medium contrast) developed for 10 min in D-19 developer diluted 1:1, 0.40–0.44-μA beam currents, 35–120-s exposure times, 0.05662–0.05665-Å electron wavelengths, and nozzle-to-plate distances of 752.77 and 296.78 mm. Data were obtained from four plates at each distance in the usual way,[10,11] and computer-generated backgrounds were subtracted.[12] The useful data covered the range $2.00 \leq s \leq 12.50$ Å^{-1} and $6.50 \leq s \leq 31.25$ Å^{-1} in intervals $\Delta s = 0.25$ Å^{-1} ($s = 4\pi\lambda^{-1} \sin(\theta/2)$; θ is the scattering angle). Curves of the levelled total intensity s^4I_T and the final

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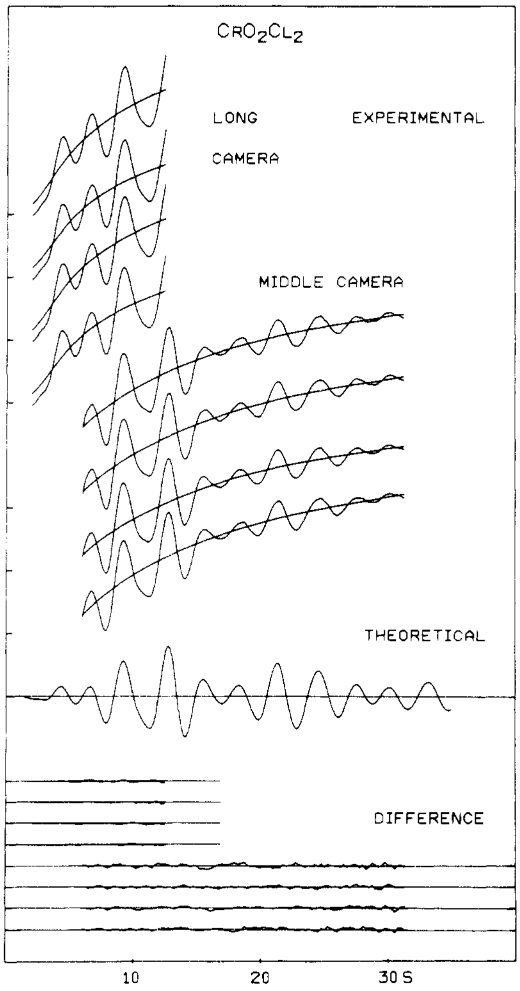

Figure 1. Intensity curves. The experimental curves are s^4I_T shown superimposed on the calculated backgrounds. The theoretical curve corresponds to model A of Table I. Difference curves are experimental minus theoretical.

backgrounds are shown in Figure 1; the data are available as supplementary material.

Calculations of intensity curves and radial distribution curves were done using eq 1 and 2. In eq 1, the modified scattering amplitudes

$$sI_m(s) = k\sum_{i\neq j} n_{ij}A_iA_jr_{ij}^{-1}\exp(-l_{ij}^2s^2/2)\cos(\eta_i - \eta_j)\sin s(r_{ij} - \kappa_{ij}s^2) \quad (1)$$

$$rD(r) = (2/\pi)\,\Delta s\sum_{s=0}^{s_{\max}} I'(s)\exp(-Bs^2)\sin rs \quad (2)$$

$A(s) = s^2|f(s)|$ and the phases $\eta(s)$ were obtained from tables[13] as previously described.[10] Values of κ were estimated to be 0.85×10^{-6} and 2.0×10^{-6} Å^3 for the Cr═O and Cr—Cl distances, respectively, and assumed to be 0 for others. In eq 2, $I'(s)$ was set equal to $sI_m(s)Z_{Cr}Z_{Cl}A_{Cr}^{-1}A_{Cl}^{-1}$ and the coefficient B was given the value 0.0025 Å^2. For the experimental $rD(r)$ curves theoretical intensity data were used in the unobserved small angle range $s < 2.00$ Å^{-1}.

Structure Analysis

The positions of the five peaks in the experimental radial distribution curve correspond to the five interatomic distances expected for a CrO_2Cl_2 molecule of C_{2v} symmetry. With this symmetry the structure is defined by four geometrical parameters and may be refined in terms of any convenient set such as the two bond lengths and a pair of bond angles. A second mode of refinement is also possible: because the individual distances are well resolved, they may be refined directly without the imposition of the symmetry constraint. Without certain distance corrections, the results of these two types of refinements will differ slightly because of averaging effects arising from molecular vibration. (r_a values for distances refined independently are usually slightly smaller than values calculated from r_a bond lengths applying symmetry constraints; the differences are termed shrinkage.) For CrO_2Cl_2 a rather considerable amount of vibrational spectroscopic data leads to a good force field from which corrections might be obtained. Comparison of the results from the two refinement modes affords an experimental check of the spectroscopically derived corrections.

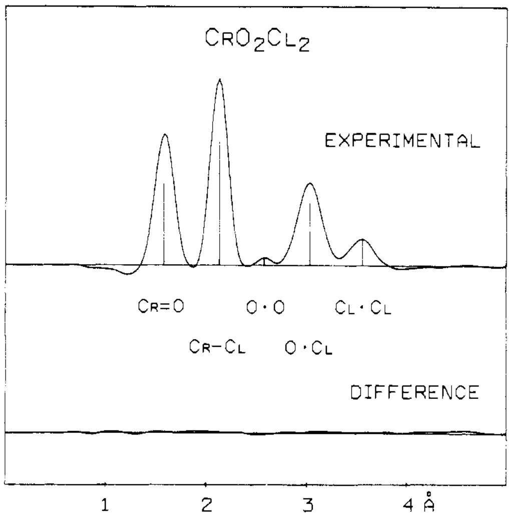

Figure 2. Radial distribution curves. The experimental curve is calculated from a composite of the molecular intensities from the two camera distances. The vertical lines indicate the positions and weights of the distances in the preferred model. The difference curve is experimental minus theoretical.

The set of interatomic distances calculated from the thermal average atomic *positions* in a molecule-fixed coordinate system (r_α) are related to the r_a distances used in eq 1 by the formulas given in eq 3. The correction terms K (perpendicular amplitude corrections) and δr (centrifugal distortions) were calculated from the force field discussed below; the l's (root-mean-square amplitudes of vibration) were given the experimental values obtained in the course of refinement. The four geometrical parameters consistent with C_{2v} molecular symmetry for CrO_2Cl_2 were taken as r_α(CrO), r_α(CrCl), $\angle_\alpha$OCrO, and $\angle_\alpha$ClCrCl. Refined values for these and for the five root-mean-square amplitudes of vibration (l) were determined by least squares, fitting a single theoretical curve calculated according to eq 1 to the eight experimental intensity curves. A unit weight matrix was used. The fitting procedure converged rapidly to give largely uncorrelated values for both the geometrical parameters and the amplitudes of vibration. The results are designated in Table I as model A.

$$\begin{aligned} r_a &= r_g - l^2/r_\alpha \\ &= r_\alpha + K + \delta r - l^2/r_\alpha \end{aligned} \quad (3)$$

The parameters for the refinement without geometrical constraint were the five interatomic distances and the five corresponding amplitudes of vibration. The results are listed in Table I as model B; they are virtually identical with those for a different type of model, C, which is discussed below.

Although the agreement between the r_a distances of models A and B is very good, there are interesting differences between the corresponding values for the nonbonds: in particular, that for O···O at 0.005 Å is rather larger than all the others. It seemed possible that the larger O···O difference was a re-

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Table I. Structural Results for Models of CrO_2Cl_2[a,b]

	model A[c]				model B		model C		Palmer[d]
parameter	r_α or $\angle_\alpha$	r_g	r_a	l	r_a	l	r_a or $\angle_\alpha$	l	r
Cr=O	1.577 (2)	1.581 (2)	1.580 (2)	0.047 (2)	1.580 (2)	0.047 (2)	1.580 (2)	0.047 (2)	1.57 (3)
Cr–Cl	2.122 (2)	2.126 (2)	2.124 (2)	0.053 (2)	2.124 (2)	0.053 (2)	2.124 (2)	0.053 (2)	2.12 (2)
O···O	2.559 (8)	2.564 (8)	2.562 (8)	0.070 (8)	2.567 (10)	0.071 (8)	2.567 (10)	0.071 (8)	2.49 (10)
O···Cl	3.023 (4)	3.026 (4)	3.023 (4)	0.091 (4)	3.024 (4)	0.091 (4)	3.024 (4)	0.091 (4)	3.03 (3)
Cl···Cl	3.545 (7)	3.547 (7)	3.544 (7)	0.105 (7)	3.545 (8)	0.104 (7)	3.545 (8)	0.104 (7)	3.54 (5)
∠OCrO	108.5_1 (4_3)						108.7_3 (5_4)		105 (4)
∠ClCrCl	113.2_9 (3_2)						113.2_7 (3_2)		113 (3)
∠OCrCl	108.7_4 (1_1)						108.6_9 (1_3)		109 (3)
factor[e]	[1.0][f]						0.55 (46)		
R[g]	0.0568				0.0566		0.0566		

[a] Distances (r) and amplitudes (l) in Å; angles in degrees. See text for definition of distance types. [b] Parenthesized numbers are 2σ uncertainties including estimates of systematic error and correlation. [c] Preferred model. [d] Reference 9. [e] Fraction of calculated shrinkages included. [f] Not refined. [g] $R = \Sigma_i w_i \Delta_i^2 / \Sigma_i w_i (s_i I^{\mathrm{obsd}}(s))^2$ where $\Delta_i = s_i I_i^{\mathrm{obsd}}(s) - s_i I_i^{\mathrm{calcd}}(s)$.

Table II. Correlation Matrix (× 100) for Model A of CrO_2Cl_2

	r(CrO)	r(CrCl)	∠OCrO	∠ClCrCl	l(CrO)	l(CrCl)	l(OO)	l(OCl)	l(ClCl)
σ_{LS}[a]	0.029	0.018	15.3	11.4	0.039	0.024	0.278	0.066	0.180
	100	−5	6	9	4	10	−2	−2	2
		100	12	−5	−4	−6	−7	−2	−4
			100	−36	<1	2	−8	−9	1
				100	−5	−5	1	7	<1
					100	50	2	15	7
						100	−4	20	8
							100	−2	1
								100	−4
									100

[a] Standard deviation not including estimates of correlation or systematic effects. Distances and amplitudes are given in Å and angles are in degrees.

flection of errors in the calculated corrections applied to model A. It is not possible to check the corrections directly, only the shrinkages which are their consequence. A reasonable assumption concerning the shrinkages is that the calculated values are wrong in magnitude but right in ratio. (A similar assumption is often made in group refinement of amplitudes of vibration.) Model C was designed to investigate the matter. This model was based on C_{2v} symmetry, and the structural parameters were the two r_a bond lengths, the bond angles OCrO and ClCrCl, and a scale factor for the shrinkages. The ratio of the shrinkages was maintained at the calculated values.

The values of the quality-of-fit factor R for the models just described do not differ significantly. We adopt model A as an appropriate representation of the structure. The correlation matrix for this model is given in Table II; the correlation matrices for the other models are similar.

Harmonic Force Field

Varetti and Müller[14] (V–M) have recently analyzed the infrared spectrum of several isotopes of CrO_2Cl_2 in an argon matrix. Using these data, together with the gas-phase infrared frequencies[15] and Palmer's structure,[9] they determined values for many of the quadratic force constants. Our interest in the force field stemmed from the need for the quantities used to interconvert the distance types r_a, r_g, r_α. We first re-refined the quadratic force constants using (as did V–M) Shimanouchi and Suzuki's[16] symmetry coordinates together with the gas-phase frequencies, V–M's isotopic data, and our structure instead of Palmer's. The final results, based on our model A, differ slightly (but hardly significantly) from V–M's. The two sets of force constant values are given in Table III, the force constant correlation matrices from our refinement in Table IV, and the agreement between calculated and observed frequencies and shifts from our results in Table V. Our results were used to calculate the values of δr, K, and l collected in Table VI.

Table III. Values of Symmetry Force Constants for CrO_2Cl_2[a]

			this investigation[b]	V–M[c,d]
A_1	F_{11}	F_{CrO}	7.656 (6)	7.54
	F_{22}	F_{CrCl}	2.815 (10)	2.88
	F_{33}	F_{OCrO}[e]	1.219 (5)	1.22
	F_{44}	F_{ClCrCl}[e]	0.488 (3)	0.48
	F_{12}		[0.25][f]	0.25
	F_{13}		[0.20][f]	0.20
	F_{23}		[0.08][f]	0.08
A_2	F_{55}	F_{OCrCl}	0.610	0.60 (10)
B_1	F_{66}	F_{CrO}	6.764 (39)	6.76 (12)
	F_{77}	F_{OCrCl}	0.682 (3)	0.70 (2)
	F_{67}		0.157 (65)	0.00 (20)
B_2	F_{88}	F_{CrCl}	2.450 (29)	2.42 (16)
	F_{99}	F_{OCrCl}	0.694 (8)	0.68 (5)
	F_{89}		0.050 (16)	0.04 (9)

[a] Units are aJ $Å^{-2}$ for stretches, aJ rad^{-2} for bends, and aJ $Å^{-1}$ rad^{-1} for stretch–bend interactions. [b] Uncertainties are σ. [c] Reference 14. [d] Statistical nature of uncertainties not specified. [e] These symmetry coordinates involve other angles as well. The main contribution is from the angle which is listed. [f] Assumed.

Table IV. Correlation Matrix (× 100) for CrO_2Cl_2 Force Field

	A_1				B_1			B_2		
	F_{11}	F_{22}	F_{33}	F_{44}	F_{66}	F_{77}	F_{67}	F_{88}	F_{99}	F_{89}
σ	0.06	1.0	0.5	0.3	3.9	0.2	6.5	2.9	0.8	1.6
	100	−3	1	−2	100	−33	99	100	−96	99
		100	−77	−4		100	−33		100	−95
			100	1			100			100
				100						

Discussion

The first electron-diffraction study of CrO_2Cl_2 was done over 40 years ago with noninstrumental methods for measurement of ring diameters and scattered intensities. The results of that study are listed in Table I and are seen to be in excellent

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Table V. Observed and Calculated Vibrational Wave Numbers and Isotopic Shifts for CrO_2Cl_2

		frequencies[a]		isotopic shifts[b,c]									
		$^{52}Cr^{16}O_2{}^{35}Cl_2$		$CrO_2Cl^{37}Cl$		$CrO_2{}^{37}Cl_2$		$^{50}CrO_2Cl_2$		$^{52}CrO_2Cl_2$		$^{54}CrO_2Cl_2$	
		obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
A_1	ν_1	991	991.0							−2.3	−1.8		
	ν_2	470	470.6	−2.8	−2.7	−5.2	−4.9						
	ν_3	355.8	355.1	−1.7	−1.9	−3.9	−3.9						
	ν_4	139.2	139.2										
A_2	ν_5	224	224.0										
B_1	ν_6	1002	1002.0					5.8	5.8	−2.7	−2.8	−5.5	−5.4
	ν_7	212	212.0										
B_2	ν_8	502.7	502.7	−2.7	−2.5	−5.4	−5.5						
	ν_9	257	257.0										

[a] Observed values from ref 15. [b] Observed values from ref 14. [c] Formulas designate atoms differing from parent molecule.

Table VI. Root-Mean-Square Amplitudes of Vibration (l), Perpendicular Amplitude Corrections (K), Centrifugal Distortions (δr), and r_a Shrinkages at 22 °C

				shrinkages/Å	
	l_{calcd}/Å	K_{calcd}/Å	δr_{calcd}/Å	model A[a]	model C
Cr=O	0.0375	0.0044	0.0001		
Cr–Cl	0.0464	0.0029	0.0007		
O···O	0.0674	0.0049	-0.0000_3	0.0023	0.0013
O···Cl	0.0899	0.0023	0.0008	0.0041	0.0023
Cl···Cl	0.1101	0.0005	0.0013	0.0051	0.0028

[a] Calculated values.

agreement with ours: in no case does our much more precise value for a parameter differ from the early one by more than the associated "limit of error". It is worth remarking that such favorable comparisons are more the rule than the exception and attest to the care and skill the early workers brought to their task.

As a basis for judging the character of the bonds in the CrO_2Cl_2 molecule, we may take the Schomaker–Stevenson radius for oxygen and the Pauling radii for chlorine and chromium.[17] With the usual correction for electronegativity difference, the prediction is about 2.11 Å for the length of a Cr—Cl single bond and 1.56 Å for a Cr=O double bond. These are both close to the observed values an accordingly we conclude that Cr—Cl and Cr=O in CrO_2Cl_2 are respectively essentially pure single and pure double bonds. Since the metal atom in CrO_2Cl_2 is formally d^0, one might expect that the bond angles would be successfully predicted by VSEPR theory. Our verification of the result ∠ClCrCl > ∠OCrO in CrO_2Cl_2 underscores the fact mentioned above that the theory cannot be used to obtain reliable predictions of the structures of transition-metal complexes and contrasts strikingly with its success when applied to main-group oxide halides such as SO_2Cl_2, where the bond angles (∠OSO $\simeq$ ∠ClSCl + 23°)[18] are successfully rationalized. We see no ready explanation for this failure.

Our three models have r_a distances which differ by insignificant amounts judged by the associated uncertainties and the nearly identical values of the R factors. It follows that the differences between the shrinkages, or corrections for vibrational effects applied to the nonbond distances in models A and C, cannot in themselves affect the choice of model. Our results for model C, however, do reveal an interesting point: because it was possible to bring *all* r_a distances into essentially perfect agreement with the independently refined values (model B) through use of a scaling factor applied to the group of shrinkages, the calculated values appear to be too large. This may arise from too large vibrational corrections for the bonds and/or too small corrections for the nonbonds. Our approach to the problem may be required in sensitive work with other molecules.

It has been shown[7] that approximate values for bond angles in molecules such as CrO_2Cl_2 may be derived from isotopic shifts of suitable vibrational modes. Using V–M's data,[14] we obtain ∠OCrO ≈ 109° with a strictly experimental uncertainty of about 4°, but the value for ∠ClCrCl is imaginary. The OCrO angle value obtained by this method (which assumes separability of the high and low frequencies) is in surprisingly good agreement with our electron-diffraction value. Since the bending modes and the Cr–Cl stretches are not so far apart in frequency, the poor result for ∠ClCrCl is not unexpected.

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Registry No. CrO_2Cl_2, 14977-61-8.

Supplementary Material Available: Tables of the total intensities, the final backgrounds, and the molecular intensities (12 pages). Ordering information is given on any current masthead page.

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