indicates that the dπ bonding from the replaced ligand has been nearly entirely shifted to the remaining nitrosyls, strengthening the Mn–N bonds relative to the Cr–N bonds. Formation of the iron compound from the manganese compound, and subsequently the cobalt from the iron, by the same mechanism has similar consequences. In these cases, however, the competitive advantage of nitrosyls over carbonyls has been reduced first from 3:1 to 2:2, and then to 1:3, which results in a more equitable distribution of the "excess" dπ bonding and leads to increases in the bond orders of both types of ligands.

It is notable that in the isoelectronic series under discussion the M–N bond orders are substantially greater than the M–C bond orders for the three molecules in which they coexist and the Cr–N bond order is substantially greater than the Ni–C bond order. These facts leave no doubt that a nitrosyl group is a much better π-electron acceptor than is a carbonyl group. Jolly and coworkers[2,20] have discussed the back-bonding to, and π-acceptor properties of, nitrosyl and carbonyl ligands on the basis of studies of carbon, nitrogen, and oxygen core binding energies from XPS experiments and ligand-stretching force constants. Among their conclusions are that the NO groups are much better π acceptors than CO, that the back-bonding to the CO groups diminishes only slightly from $Ni(CO)_4$ to $Fe(CO_2(NO)_2$ and then much more in the step to $MnCO(NO)_3$, and that the total amount of back-bonding increases from $Ni(CO)_4$ to $Cr(NO)_4$ in the series. These conclusions are completely consistent with ours. However, their data are also reported to be consistent with increasing back-bonding to the NO groups as the atomic number of the metal decreases whereas ours clearly are not.

Finally, it should be emphasized that it is the relative values of the M–N and M–C bond orders in Table VII and their trends from compound to compound that have significance, not the values themselves. The latter are very sensitive functions of the radii used to calculate them and hence are unreliable. The values given in the table seem reasonable, however, because they are consistent with the principle that the charges on the central atoms not be greater than unity. For example, a bond order sum of 7.5 corresponds to a formal charge of 0.5– on the metal atom, which is reduced by electron flow to the ligands impelled by the metal–ligand electronegativity difference. In the case of $Cr(NO)_4$ an assumed electronegativity difference of 1.4 corresponds to about 38% ionic character for the Cr–N bonds and hence to a net charge of about 1.0+ on chromium. A similar calculation for $Ni(CO)_4$ (with a bond order sum of 6.5) leads to a residual charge of about 1.0– on nickel. Values for the other compounds lie between these.

Acknowledgment. This work was supported by National Science Foundation Grants CHE78-04258 and CHE81-10541 to Oregon State University and by a grant to the University of Texas from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $Cr(NO)_4$, 37355-72-9; $Mn(CO)(NO)_3$, 14951-98-5; $Fe(CO)_2(NO)_2$, 13682-74-1.

Supplementary Material Available: Tables of the force field and symmetry coordinates for $Fe(CO)_2(NO)_2$ and the total scattered intensities, calculated backgrounds, and averaged molecular intensities for each substance (23 pages). Ordering information is given on any current masthead page.

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Structure and Bonding in Transition-Metal Carbonyls and Nitrosyls. 2. Gas-Phase Electron Diffraction Reinvestigation of Tricarbonylnitrosylcobalt

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Received October 26, 1984

The structure of gaseous $Co(CO)_3NO$ has been studied at room temperature. As with the data for the other $M(CO)_n(NO)_{4-n}$ compounds of the first transition group,[16] the data are completely consistent with linear MYO groups although small deviations from linearity cannot be ruled out. Values of the bond distances (r_g) and bond angles ($\angle_\alpha$) based on C_{3v} symmetry, with estimated 2σ uncertainties, are $r(\text{Co—N}) = 1.671$ (6) Å, $r(\text{Co—C}) = 1.843$ (3) Å, $r(\text{N=O}) = 1.180$ (14) Å, $r(\text{C=O}) = 1.136$ (4) Å, $\angle\text{NCoC} = 107.7$ (14)°, and $\angle\text{CCoC} = 111.2$ (13)°; the values reflect corrections for the effects of vibrational averaging (shrinkage) and anharmonicity.

Introduction

Transition-metal complexes with nitric oxide ligands (nitrosyl complexes) have structures in which the MNO groups tend to be either nearly linear or rather strongly bent. On the chemical side, these structures have been respectively interpreted as the consequence of a reaction wherein the ligand has acted as a base (NO^+) or an acid (NO^-) according to the character of the metal center. More recently, theoretical considerations have provided an understanding of the structure of the MNO groups in terms of molecular orbital models that depend on the coordination and number of d electrons of the metal, with suitable perturbations related to the σ and π type interactions of the other ligands. Several discussions of bonding models[2–6] as well as excellent review articles[6–8] of the chemical and structural literature in this area are available.

Tricarbonylnitrosylcobalt ($Co(CO)_3NO$) is a d^{10} or $\{MNO\}^{10}$ complex; the latter symbolism, suggested by Enemark and Feltham,[6] designates the number of 3d electrons in the metal plus one from the π^* orbital of each NO ligand. According to theory for such tetrahedrally coordinated complexes, the MNO groups will be linear or bent[2,3,6] depending on the relative energies of the $4a_1$ (z^2, σ(NO)) and 4e (xz, yz, π^*(NO)) orbitals—energies that are more difficult to predict than for systems in which the σ and π perturbations due to ancillary ligands are more clearly separated

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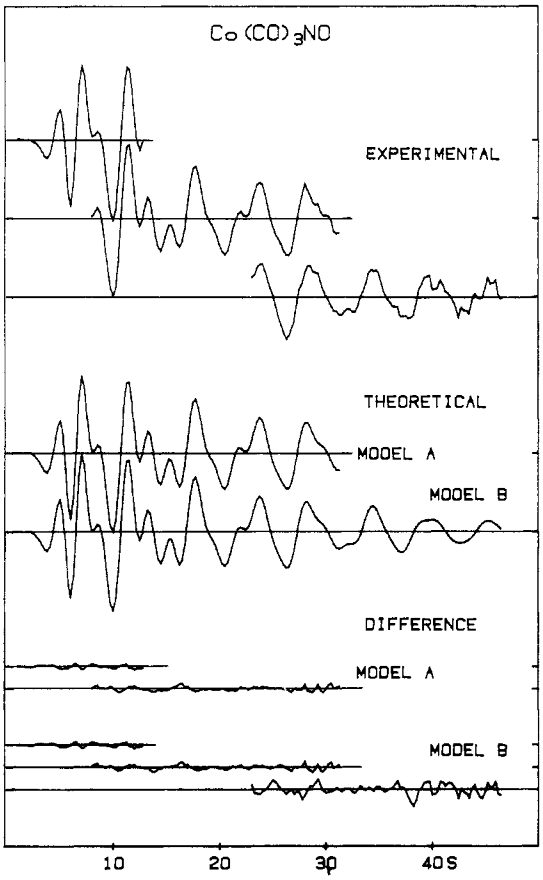

Figure 1. Intensity curves $sI_m(s)$: experimental, averages from the long and middle camera distances and data from a single plate at the short camera distance; theoretical, from models of Table I; difference, experimental minus theoretical.

by symmetry. Although many examples of bent MNO groups exist for four-coordinate $\{MNO\}^{10}$ complexes,[8] it was generally assumed that those with C_{3v} symmetry for the ML_3 fragment were linear until the recent discovery of a rather strongly bent RhNO group in $Rh(NO)(PPh_3)_3$.[9] We decided to investigate the structure of $Co(CO)_3NO$ by electron diffraction primarily because of the MNO angle question. Although a small deviation from linearity doubtless could not be detected, a severely bent group would probably be revealed in the data. Results from an exhaustive vibrational spectroscopic study[10] were expected to be of help in the calculation of the effects of vibrational averaging that, unaccounted for, would increase the uncertainties about the angle values. Finally, regardless of the MNO angle question, we expected to obtain much more precise values for bond lengths and bond angles at the metal atom than were available from an early electron diffraction investigation[11] of $Co(CO)_3NO$ based on visual estimates of intensities. Tetrahedral angles at the metal atom and linear CoYO groups were assumed in the early study and found to be consistent with the observations, but even relatively large deviations could not have been detected at that time by the visual method.

The work described here was brought to completion before the opportunity to carry out similar studies of $Cr(NO)_4$, $MnCO(NO)_3$, and $Fe(CO)_2(NO)_2$ arose. During the course of the latter work,[16] a few additional refinements of the $Co(CO)_3NO$ structure were carried out under conditions comparable to those used for the other compounds in order to have a more uniform base for comparisons. These conditions included use of the same vibrational corrections and elimination of high-angle data not available for the other molecules.

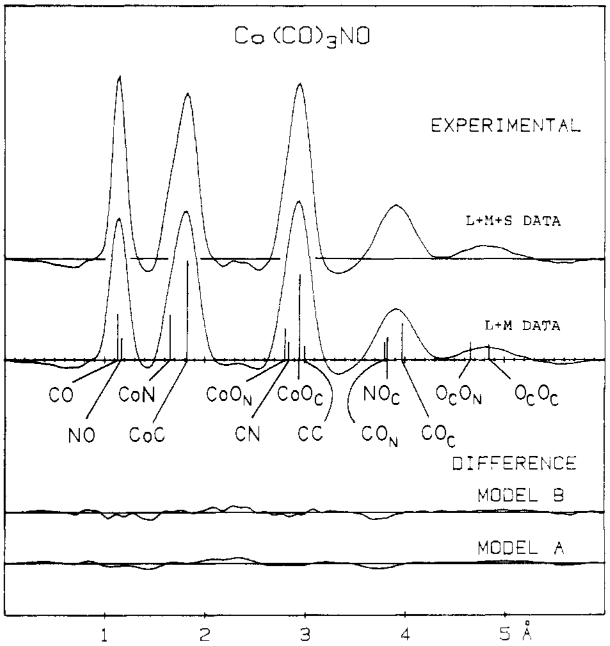

Figure 2. Radial distribution curves: experimental, data from long, middle, and short camera distances and from long and middle camera distances only; difference, experimental minus theoretical for models of Table I. Distances and relative weights are indicated by vertical bars.

Experimental Section

The sample of $Co(CO)_3NO$ was prepared as previously described[10] after the method of Mond and Wallis.[12] Exposures were made on Kodak lantern slide medium-contrast plates (8 in. × 10 in.) that were developed for 10 min in Kodak D-19 developer diluted 1:1. Nominal nozzle-to-plate distances were 750, 300, and 120 mm; exposure times were respectively 45–75, 90–150, and 420 s with beam currents of 0.25–0.40 μA. The ambient pressure in the apparatus during exposure of the plates was $(1.5\text{–}3.0) \times 10^{-5}$ torr. Three plates from the long, two from the intermediate, and one from the short camera distance were selected for analysis. Reduction of the data, removal of the backgrounds, and calculation of theoretical intensities and radial distributions of distances were done in a fashion similar to that described in the preceding article.[16] Curves of the averaged intensities from each camera distance ($sI_m(s)$) are shown in Figure 1. These averages together with the data from each plate are available as supplementary material.

Structure Analysis

For reasons given in the preceding article[16] the structure was defined in terms of r_α parameters. Vibrational corrections were first calculated from the force field of Jones et al.[10] and then from one differing slightly from it in such a way as to resemble the $Ni(CO)_4$ force field[13] as nearly as possible. Corresponding values from the two sets were virtually identical and very near the values used for the chromium, manganese, and iron compounds. For consistency we chose the same values for the vibrational corrections as were used for the other molecules.

The geometrical parameters were chosen as $\langle CO,NO\rangle = (3r_\alpha(C{=}O) + r_\alpha(N{=}O))/4$, $\Delta(CO,NO) = r_\alpha(C{=}O) - r_\alpha(N{=}O)$, $\langle CoC,CoN\rangle$ and $\Delta(CoC,CoN)$ (similarly defined), $\angle_\alpha CCoN$, and $\angle_\alpha CoNO$. The $Co(CO)_3$ group was assumed to have C_{3v} symmetry and the CoCO group to be linear, consistent with the appearance of the radial distribution curve (Figure 2). Six amplitude group parameters were formed. Amplitude differences within a group were fixed at the values used for the chromium, manganese, and iron compounds. Although these differences do not agree exactly with those calculated from the force field, the deviations are not regarded as serious in the face of uncertainties connected with other assumptions. The amplitude groups are evident from Table I. The least-squares refinements were based on the average curves shown in Figure 1. It was quickly apparent

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Table I. Structural Results for $Co(CO)_3NO^a$

param^d	model A^b				model B^c					
	r_α, $\angle_\alpha$	r_g	r_a	l^e	r_α, $\angle_\alpha$	r_g	r_a	l^e	l(calcd)^f	$K + \delta r^g$
⟨CO,NO⟩	1.128 (2)				1.128 (2)					
Δ(CO,NO)	−0.027 (21)				−0.044 (17)					
⟨CoC,CoN⟩	1.786 (3)				1.787 (3)					
Δ(CoC,CoN)	0.171 (5)				0.173 (5)					
∠NCoC	108.7 (23)				107.7 (14)					
∠CCoC	110.2 (22)				111.2 (13)					
C=O	1.121 (5)	1.140	1.139	0.038 } (4)	1.117 (4)	1.136	1.135	0.034 } (5)	0.034	0.019
N=O	1.148 (16)	1.167	1.165	0.041	1.161 (14)	1.180	1.179	0.037	0.035	0.019
Co−C	1.829 (3)	1.842	1.840	0.057 } (4)	1.830 (3)	1.843	1.841	0.058 } (4)	0.057	0.013
Co−N	1.658 (5)	1.671	1.669	0.052	1.658 (6)	1.671	1.669	0.053	0.043	0.013
Co·O_C	2.950 (5)	2.971	2.970	0.059 } (7)	2.947 (5)	2.968	2.967	0.060 } (6)	0.056	0.021
Co·O_N	2.805 (18)	2.826	2.825	0.062	2.818 (16)	2.839	2.838	0.062	0.047	0.021
C·C	3.001 (42)	3.010	3.007	0.086 } (16)	3.020 (25)	3.029	3.027	0.080 } (13)	0.132	0.009
C·N	2.835 (38)	2.844	2.842	0.086	2.818 (25)	2.827	2.825	0.080	0.168	0.009
C··O_C	3.972 (49)	3.985	3.979	0.154 } (34)	3.992 (28)	4.005	4.000	0.139 } (30)	0.165	0.013
C··O_N	3.809 (34)	3.822	3.815	0.154	3.799 (23)	3.812	3.807	0.139	0.200	0.013
N··O_C	3.819 (48)	3.832	3.826	0.154	3.795 (35)	3.808	3.803	0.139	0.196	0.013
O_C···O_C	4.840 (62)	4.853	4.838	0.272 } (70)	4.863 (35)	4.876	4.862	0.263 } (84)	0.230	0.013
O_C···O_N	4.678 (55)	4.691	4.675	0.272	4.656 (35)	4.669	4.654	0.263	0.257	0.013
R^h	0.057				0.087					

[a] Distances (r) and amplitudes (l) in angstroms; angles (∠) in degrees. Quantities in parentheses are estimated 2σ. [b] Refinement without short camera data. [c] Preferred model; refinement with short camera data included. [d] See text for definitions. [e] Quantities in braces refined as groups. [f] From force field of ref 8. [g] Vibrational corrections; see preceding article.[16] [h] $R = |\Sigma w_i \Delta_i^2 / \Sigma_i w_i (s_i I_i(\text{obsd}))^2|^{1/2}$, where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

Table II. Correlation Matrix (×100) for $Co(CO)_3NO$, Model B

	σ^a	$\langle r\rangle_1$	Δr_1	$\langle r\rangle_2$	Δr_2	$\angle_1$	$\angle_2$	l_1	l_2	l_3	l_4	l_5	l_6
⟨CO,NO⟩	0.062	100											
Δ(CO,NO)	0.603	−66	100										
⟨CoC,CoN⟩	0.080	−17	−8	100									
Δ(CoC,CoN)	0.193	19	−19	−41	100								
$\angle_\alpha$CCoN	50.5	−49	82	−17	15	100							
$\angle_\alpha$CCoC	47.1	49	−82	17	−15	−100	100						
l(C═O)	0.151	−57	89	−17	−3	73	−73	100					
l(Co—C)	0.108	12	−4	−17	34	5	−5	11	100				
l(Co·O_C)	0.198	−27	52	−15	15	74	−74	53	19	100			
l(C·C)	0.461	−54	47	−10	14	45	−45	50	19	45	100		
l(C··O_C)	1.05	−34	70	−15	12	96	−86	64	6	68	42	100	
l(O_C··O_C)	2.94	−41	13	−3	3	15	−14	12	2	12	19	49	100

[a] Standard deviations from least squares (×100); distances and amplitudes in angstroms and angles in degrees.

that our data held no definite evidence for nonlinearity of the CoNO group, for regardless of the trial value of this angle, the shifts after a few cycles had led to a value insignificantly different from 180°. The final refinements were carried out with the CoNO angle assumed to be linear.

The final results listed as model A in Table I were obtained without use of the data from the single short camera plate. Model B is the set of results obtained with inclusion of these data; the relative weighting was 4:4:1 for the long:intermediate:short distance data. Anharmonicity coefficients were given values of 1.4×10^{-6} Å^3, 0.9×10^{-6} Å^3, 3.5×10^{-6} Å^3, and 2.4×10^{-6} Å^3, respectively, for the C═O, N═O, Co—C, and Co—N bonds and were ignored for nonbond distances. Since the two values for each parameter, taking into account their uncertainties, are in very good agreement, either model is a satisfactory expression of the structure of $Co(CO)_3NO$. We adopt model B as our final model in view of the greater number of data on which it is based. Table II is the correlation matrix for the more important parameters.

Discussion

Because the nonbond distance in a linear CoNO group changes very little with change in angle (e.g., about 0.018 Å for 10°), it is impossible to distinguish quasi-linear equilibrium conformations from linear ones when the effects of molecular vibration are present. Our results thus do not prove that the CoNO group is strictly linear. However, they do show that it is at least quasi-linear and rule out unequivocally a severely bent group on the order of 120°. From these results and those put forth in the preceding article, one may conclude that the MNO groups in d^{10} tetrahedrally coordinated complexes of the first transition series are linear, or very nearly so.

Brockway and Anderson's[11] (BA) early work on $Co(CO)_3NO$ led to the values r(Co–C) = 1.83 ± 0.02 Å and r(Co–N) = 1.76 ± 0.03 Å. Their Co–C value is in good agreement with ours (r_a in Table I), but their Co–N one is at least 0.05 Å too long. Since these two distances are rather accurately measured in our investigation, we conclude that BA's value for Co–N is in error. A second difference between BA's and our results concerns the relative magnitudes of the distances r(C═O) and r(N═O): whereas we find the former to be the smaller, BA report it to be the larger (1.14 ± 0.03 Å vs. 1.10 ± 0.04 Å). Although the magnitude of the difference between these bond lengths found in our investigation is highly correlated with the bond angles at cobalt (Table II), there is no doubt that r(N═O) is larger than r(C═O). The discrepancies between BA's and our results are at first sight surprisingly large, even after allowance for the primitive technique of BA's time. BA's report, however, suggests their work was not a structure determination based on the results of parameter variation but a demonstration that a model deduced from the structures of $Ni(CO)_4$ and $Fe(CO)_2(NO)_2$ (which had been more thoroughly investigated) was not inconsistent with their visually estimated intensity distribution.

The molecule $Co(SbPh_3)(CO)_2NO$ in the crystal[14] has a Co–C distance equal to 1.763 (5) Å and a Co–N distance equal to 1.698

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(5) Å, respectively, some 0.08 Å shorter and 0.03 Å longer than those we find in $Co(CO)_3NO$. These differences are the consequence of the replacement of a relatively poor π acceptor ($SbPh_3$) with a good one (CO), followed by more effective competition for the available π-bonding electrons by a still better π acceptor (NO). We note that for $Co(SbPh_3)(CO)_2NO$ the sum of the bond orders of the bonds to cobalt, calculated as described in the preceding article,[16] is 7.87, in reasonably good agreement with the value 7.33 calculated for $Co(CO)_3NO$, as is also the value 6.95 calculated for $Co(PPh_3)_2(SO_2)(NO)$.[15] The total amount of π bonding from cobalt to its ligands in d^{10} complexes thus tends to be constant.

Acknowledgment. This work was supported by the National Science Foundation under Grants CHE78-04258 and CHE81-10541.

Registry No. $Co(CO)_3NO$, 14096-82-3.

Supplementary Material Available: Tables of intensity data from each plate and averages from each camera distance (5 pages). Ordering information is given on any current masthead page.

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Dichlorotrifluorophosphorane (PCl_2F_3): Molecular Structure by Gas-Phase Electron Diffraction and Quadratic Force Field

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Received November 8, 1984

The molecular structure of gaseous PCl_2F_3 has been determined at a nozzle temperature of 22-24 °C. The chlorine atoms are found to be in equatorial sites, as predicted from other types of experiments. The values of some of the distance and angle parameters and some of the more important root-mean-square amplitudes of vibration are $r_g(P-F_e) = 1.546$ (9) Å, $r_g(P-F_a) = 1.593$ (4) Å, $r_g(P-Cl) = 2.004$ (2) Å, $\angle_\alpha(F_a-P-F_e) = 89.3$ (3)°, $\angle_\alpha(Cl-P-Cl) = 122.0$ (5)°, $l(P-F_e) = 0.052$ (8) Å, $l(P-F_a) = 0.047$ (3) Å, and $l(P-Cl) = 0.050$ (2) Å, where parenthesized quantities are estimated 2σ. Although the fluorine atoms are known to exchange at the temperature of our experiment, presumably by a Berry type mechanism that would generate isomers with chlorine atoms in axial positions, the diffraction data give no reliable indication of the presence of such isomers; neither, however, can small amounts be ruled out. Details of the structure are discussed.

Introduction

Pentacoordinated molecules having more than one type of ligand may exist in several stereoisomeric forms. In many of these molecules with fluorine atoms in both equatorial and axial sites—examples are $PF_3(NH_2)_2$, $PClF_4$, and PCl_2F_3, as well as PF_5 itself—the fluorine atoms are known to exchange. A possible mechanism for such exchange is the well-known Berry inversion,[2] which, in the case of PF_5, may be visualized as an increase of one of the equatorial angles from 120 to 180° accompanied by a simultaneous movement of the (former) axial fluorines into the gap. The detailed dynamics of the process are not well understood, but it appears[3] that the motion must be characterized in the classical sense as "flipping" rather than "flowing".

An interesting subject for study of inversion dynamics is the molecule PCl_2F_3. The distances involving the chlorine atoms are longer and are of greater weight than those involving fluorines at corresponding sites, so that identification of possible isomers from electron-diffraction measurements should be straightforward. In turn, both the kinds of isomers and the mixture composition are connected to the mechanism of the exchange process.

An early electron diffraction investigation of PCl_2F_3 by the "visual" method has been reported,[4] from which it was deduced that the chlorine atoms were located in the axial positions of a trigonal bipyramid. However, later NMR,[5,6] NQR,[6] infrared,[7,8] and Raman[7a] evidence points strongly to a molecule with equatorially sited chlorine atoms as the principal isomer. The electron-diffraction investigation reported here was undertaken to explore the questions of isomeric composition as well as to measure the values of the principal structural parameters.

Experimental Section

The sample of PCl_2F_3 was prepared as follows. To a 1-L Pyrex round-bottom bulb were added PF_3 (10 mmol) and anhydrous Cl_2 (9.5 mmol) at −196 °C. The reaction mixture was allowed to warm slowly and to remain at 25 °C for 1 h. The mixture was purified by a trap-to-trap distillation where the pure PCl_2F_3 was retained at −95 °C after having passed through a trap at −78 °C. The entire system had been carefully dried before any operation began. The purity of the compound was confirmed by infrared[7,8] and ^{19}F and ^{31}P NMR[6] spectroscopy. The spectra agreed with those in the literature.

The diffraction experiments were carried out in the Oregon State apparatus with the nozzle tip at 22-24 °C. Because PCl_2F_3 is readily hydrolyzed, the nozzle was first heated for 2 h at 200 °C under vacuum and then seasoned by a stream of sample to remove adsorbed water vapor. Conditions of the experiments were an r^3 sector, electron wavelengths of 0.054 95-0.054 99 Å (calibrated against CO_2 in separate experiments: $r_a(C{=}O) = 1.1646$ Å, $r_a(O{\cdot}O) = 2.3244$ Å), camera distances of 746.9 and 300.9 mm, exposure times of 70-189 s, 8 × 10 in. Kodak projector slide plates (medium), and development in Kodak D-19 developer diluted 1:1 for 10 min. Scattered intensity data were obtained in the usual way[9,10] from three plates made at each camera distance. Computer-generated backgrounds were subtracted,[11] and the result was multiplied by s ($s = 4\pi\lambda^{-1} \sin\theta$; 2θ is the scattering angle) to give useful molecular intensity data in the form[9] $sI_m(s)$ over the ranges $2.00 < s < 13.00$ Å^{-1} and $6.00 < s < 31.75$ Å^{-1} from the longer and shorter camera distances, respectively. Curves of the intensity data are shown in Figure 1. The data are available as supplementary material.

Radial Distribution. Figure 2 shows the final radial distribution of distances in PCl_2F_3 calculated in the usual way[9] from the modified mo-

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