each, these distances have average (maximum) deviations of 0.002 Å (0.005 Å) from their average values. On the other hand, the W═Y distances vary over a rather wider range: the average (maximum) deviations from their respective averages are 0.008 Å (0.013 Å). For reasons that are unclear, the W═Y variation is unsystematic. In WSF_4 and $WSeF_4$, for example, the W═S and W═Se distances are longer than in the corresponding chloro compounds, but the W═O distance in WOF_4 is shorter than it is in $WOBr_4$ and $WOCl_4$. Unfortunately, our measurements of the W═S and W═Se distances in $WSBr_4$ and $WSeBr_4$ have relatively large uncertainties that render the distances statistically indistinguishable from those in the related fluoro and chloro compounds.

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Registry No. $WSeBr_4$, 54760-62-2; $WSBr_4$, 27388-80-3; $WOBr_4$, 13520-77-9; $WSeCl_4$, 41549-02-4; $WSCl_4$, 25127-53-1; $WOCl_4$, 13520-78-0; $WSeF_4$, 66871-85-0; WSF_4, 41831-80-5; WOF_4, 13520-79-1.

Supplementary Material Available: Tables of the total scattered intensities from each plate, the calculated backgrounds, and the averaged intensities from each camera distance (18 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Oregon State University, Corvallis, Oregon 97331,
and Portland State University, Portland, Oregon 97207

Molecular Structure of $CrO_2(NO_3)_2$ in the Gas Phase: A Novel Form of Coordination for Chromium?

Colin J. Marsden,[1a,b] Kenneth Hedberg,*,[1a] M. M. Ludwig,[1c] and Gary L. Gard[1c]

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The gas-phase molecular structure of chromyl nitrate, $CrO_2(NO_3)_2$, has been studied by electron diffraction at a temperature of 50 °C and by ab initio methods at the HF level. The diffraction data are consistent with C_2 symmetry for the molecule. The coordination about Cr is best described as derived from a severely distorted octahedron, since the nitrate groups act as bidentate ligands which are asymmetrically bonded to Cr. Chromium forms two multiple bonds to O atoms (Cr═O), two nominal single bonds to O_N atoms (Cr—O), and two very long, presumably weak (estimated bond order 0.19–0.29) bonds (Cr←O) to other O_N atoms on each of the nitrate groups. Given the doubt about the existence of CrF_6, chromyl nitrate may be the only Cr(VI) species known to be six-coordinate. Principal distances (r_g/Å) and angles (∠/deg), followed by estimated 2σ uncertainties in parentheses, are r(Cr═O) = 1.586 (2), r(Cr—O) = 1.957 (5), r(Cr←O) = 2.254 (20), r(N—O) = 1.341 (4), $r(\mathrm{N{=}O_{Cr}})$ = 1.254 (4), r(N═O) = 1.193 (4), ∠(O═Cr═O) = 112.6 (35), ∠(O—Cr—O) = 140.4 (33), $\angle(\mathrm{O{=}Cr{-}O_4})$ = 97.2 (18), $\angle(\mathrm{O{=}Cr{-}O_8})$ = 104.5 (9), ∠(O═Cr←O) = 83.7 (34), ∠(Cr—O—N) = 97.5 (5), $\angle(\mathrm{O{-}N{=}O_{Cr}})$ = 112.2 (1), ∠(O—N═O) = 119.7 (40), and ∠(O═N═O) = 128.1 (36). The Cr—O—NO_2 group is only slightly nonplanar with the dihedral angle of the planes Cr—O—N and NO_2 equal to 16 (3)°. It appears that there is relatively little torsional motion around either of the single bonds in the –O—NO_2 groups. Results of geometry optimization at the SCF level with a large all-electron basis agree reasonably well with those from the electron-diffraction experiment and strongly support the conclusions about the nature of the coordination of the Cr atom. Tests with a pseudopotential for Cr, however, led to the unreasonable value 1.40 Å for r(C═O).

Introduction

The set of rules known as valence-shell electron-pair repulsion theory (VSEPR)[2] is one of the great organizing themes of structural chemistry. While the rules are simple, they provide a foundation for predictions of molecular shapes in organic and main-group inorganic chemistry which are almost always reliable. Compounds for which the VSEPR rules fail are therefore of unusual interest. Recent work from this laboratory has shown that the bond angles in some d^0 transition-metal compounds such as CrO_2F_2[3] and CrO_2Cl_2[4] do not obey the VSEPR rules. In both these molecules, the Cr═O (formally) double bonds are less sterically demanding than the Cr–F or Cr–Cl single bonds, whereas in the analogous sulfuryl halides the O═S═O angles exceed the X–S–X angles (X = F, Cl) by more than 20°.[5,6] However, it should not be assumed that the VSEPR rules always fail for transition-metal derivatives, as $TiCl_4$ is tetrahedral[7] and MoF_6 is octahedral;[8] both of these compounds also contain d^0 metals.

Since nitrate groups have an unusually versatile coordination chemistry (no fewer than nine different coordination modes were identified in a review of nitrate complexes[9]), chromyl nitrate, $CrO_2(NO_3)_2$, poses particularly interesting structural problems over and above those associated with the VSEPR-like angular question already mentioned for the chromyl halides. In general,[9] nitrate acts as a bidentate ligand to metal ions, and its small "bite" of less than 2.2 Å allows metals to display unusually high coordination numbers; some examples include $[Co(NO_3)_4]^-$[10] and $Sn(NO_3)_4$,[11] which both have dodecahedral structures with 8-coordinate metals, and $[Y(NO_3)_5]^-$[12] with 10-coordinate[12] and $[La(NO_3)_6]^-$[13] with 12-coordinate metals. There are compounds in which all the coordinated nitrates act as monodentate ligands, such as tetrahedral $[Au(NO_3)_4]^-$[14] and others in which some of the nitrate groups are bidentate and some monodentate, such as $[Sc(NO_3)_5]_2^-$,[13] in which Sc is 9-coordinate. In bidentate examples

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[1] (a) Oregon State University. (b) Permanent address: School of Chemistry, The University of Melbourne, Parkville, Victoria 3052, Australia. (c) Portland State University.

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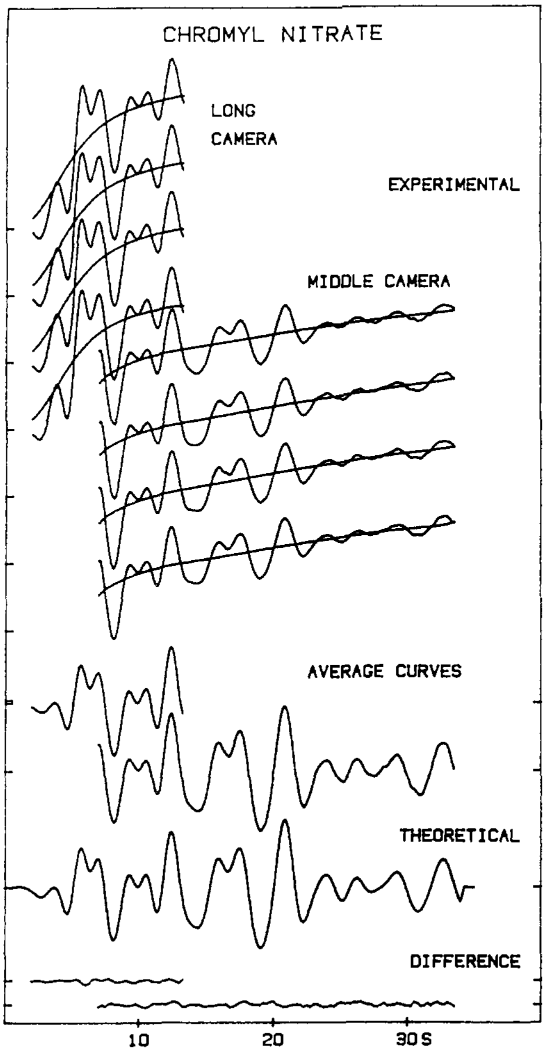

Figure 1. Intensity data for $\mathrm{CrO_2(NO_3)_2}$. Individual s^4I_t curves from each plate, magnified 7× to reveal better the molecular scattering, are shown superimposed on their backgrounds. The average curves are $s[s^4I_t - \text{bkgd}]$. The theoretical curve is for the model of Table I. The difference curves are experimental minus theoretical.

the bonding of the nitrate is quite frequently asymmetric, as for example in $[\mathrm{Co(NO_3)_4}]^-$ [10] or $\mathrm{(CH_3)_2Sn(NO_3)_2}$,[15] and the differences in the two metal–oxygen distances of one nitrate group can be as large as 0.7 Å.[9] The size of the Cr(VI) ion is very small, and thus a coordination number as high as 6 does not seem likely. Indeed, $\mathrm{CrF_6}$ appears to be the only reported example of 6-coordinate Cr(VI),[16] and the spectroscopic evidence for the existence of this compound has just been questioned.[17] Given the experience cited above, one could not predict with confidence the coordination about chromium in $\mathrm{CrO_2(NO_3)_2}$. We therefore felt that a structural study of $\mathrm{CrO_2(NO_3)_2}$ would be most worthwhile. We report here our gas-phase electron-diffraction results as well as the results of HF/SCF ab initio calculations.

Experimental Section

A sample of $\mathrm{CrO_2(NO_3)_2}$ was prepared and purified at Portland State University, following literature procedures.[18] Diffraction experiments were carried out with the Oregon State apparatus using an r^3 sector. The sample was maintained at 35–42 °C, and the nozzle at 44–51 °C. Kodak projector slide plates (8 × 10 in. medium contrast) were developed for 10 min in D-19 developer diluted 1:1. The beam current was 0.36–0.45 μA, exposure times were $1\text{–}3^1/_2$ min, nozzle-to-plate distances were 746.88 and 299.43 mm, and electron wavelengths were 0.057 15–0.057 18 Å. Data were obtained from four plates at the longer, and five plates at the shorter, camera distance following techniques already described.[19] The useful data covered the range $2.00 \leq s/\text{Å} \leq 13.25$ and $7.00 \leq s/\text{Å} \leq 33.50$, in increments of 0.25 Å^{-1}. Curves of the leveled total intensity s^4I_t and the final computer-generated backgrounds are displayed in Figure 1; the data are available as supplementary material. Intensity curves and radial distribution functions were calculated as previously described,[19] using scattering factors interpolated from tabulated values. No corrections for vibrational anharmonicity were applied to the calculated scattered intensity.

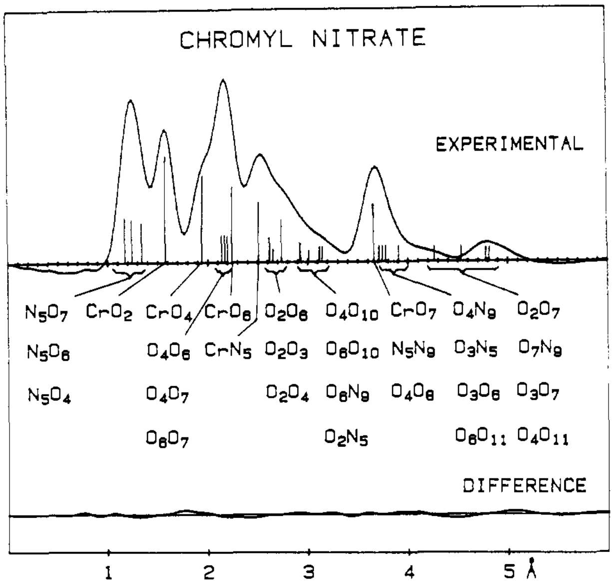

Figure 2. Radial distribution curve for $\mathrm{CrO_2(NO_3)_2}$. The vertical lines indicate the location and weights of the various internuclear distances.

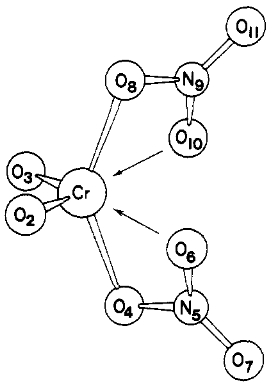

Figure 3. Perspective view of the $\mathrm{CrO_2(NO_3)_2}$ molecule, showing the atomic numbering scheme adopted.

Structural Analysis

Radial Distribution Curves. Chromyl nitrate is a rather complex molecule for a complete structure determination by electron diffraction. Fortunately, the radial distribution (RD) curve (Figure 2) has several well-resolved peaks that can be assigned with confidence to bonds and geminal distances (i.e., torsion-insensitive terms), as follows. The peak at 1.25 Å corresponds to bond distances in the nitrate group. The peak near 1.6 Å is due to chromium–oxygen multiple bonds, which may be symbolized as $\mathrm{Cr{=}O}$: typical $\mathrm{Cr{=}O}$ distances, such as those in $\mathrm{CrO_2F_2}$[3] and $\mathrm{CrO_2Cl_2}$,[4] are about 1.58 Å. Analysis of the area and shape of this peak indicates that it is derived from two and only two $\mathrm{Cr{=}O}$ distances in $\mathrm{CrO_2(NO_3)_2}$. One may predict that the length of $\mathrm{Cr^{VI}{-}O}$ single bonds will lie in the range 1.81–1.92 Å;[20] the

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Table I. Interatomic Distances (r), Angles ($\angle$, τ), and Vibrational Amplitudes (l) for $\mathrm{CrO_2(NO_3)_2}$

struct-defining params		calcd angles	
item	r/Å; $\angle$, τ/deg	item	$\angle$/deg
$r_\alpha(\mathrm{Cr{=}O})$	1.584 (2)	$\angle_\alpha(\mathrm{O_2{=}Cr{-}O_4})$	97.2 (18)
$r_\alpha(\mathrm{Cr{-}O})$	1.954 (5)	$\angle_\alpha(\mathrm{O_2{=}Cr{-}O_8})$	104.5 (9)
$r_\alpha(\mathrm{O{-}N})$	1.338 (4)	$\angle_\alpha(\mathrm{O{-}N{=}O_6})$	112.2 (71)
$\langle r_\alpha(\mathrm{N{=}O})\rangle$	1.222 (2)	$\angle_\alpha(\mathrm{O{-}N{=}O_7})$	119.7 (40)
$\Delta r_\alpha(\mathrm{N{=}O})$	0.030 (4)	$\angle_\alpha(\mathrm{O{=}N{=}O})$	128.1 (36)
$\angle_\alpha(\mathrm{O{=}Cr{=}O})$	112.6 (35)	$\angle_\alpha(\mathrm{O_2{=}Cr{\leftarrow}O_6})$	83.7 (34)
$\angle_\alpha(\mathrm{O{-}Cr{-}O})$	140.4 (33)	$\angle_\alpha(\mathrm{O_2{=}Cr{\leftarrow}O_{10}})$	160.5 (31)
$\angle_\alpha(\mathrm{Cr{-}O{-}N})$	97.5 (33)	$\angle_\alpha(\mathrm{Cr{\leftarrow}O{=}N})$	86.7 (66)
$\langle\angle_\alpha(\mathrm{O{=}N{-}O})\rangle$	116.0 (18)	$\angle_\alpha(\mathrm{O{\rightarrow}Cr{\leftarrow}O})$	82.8 (60)
$\Delta\angle_\alpha(\mathrm{O{=}N{-}O})$	−3.8 (22)	$\angle_\alpha(\mathrm{O{\rightarrow}Cr{\leftarrow}O,O{=}Cr{=}O})^a$	16.9 (16)
$\tau_\alpha(\mathrm{Cr{-}O})$	144.7 (39)		
$\tau_\alpha(\mathrm{O{-}N})$	16.0 (28)		
$\tau_\alpha(\mathrm{CrO_2})^b$	4.6 (11)		

Distances (r_g) and Amplitudes (l_α)

item	r/Å	l/Å	item	r/Å	l/Å
$\mathrm{Cr{=}O}$	1.586 (2)	0.047 (3)	$\mathrm{O_2{\cdot\cdot}O_6}$	2.626 (74)	[0.25]
$\mathrm{Cr{-}O}$	1.957 (5)	0.076 (5)	$\mathrm{O_2{\cdot\cdot}N_5}$	3.090 (39)	0.155 (45)
$\mathrm{Cr{\leftarrow}O}$	2.254 (20)	0.136 (17)	$\mathrm{O_3{\cdot\cdot}N_5}$	3.779 (27)	0.172
$\mathrm{N{=}O_6}$	1.254 (4)	0.049	$\mathrm{O_4{\cdot\cdot}N_9}$	3.724 (48)	0.172 (25)
$\mathrm{N{=}O_7}$	1.193 (4)	0.044 (5)	$\mathrm{O_3{\cdot\cdot}O_6}$	3.776 (26)	0.172
$\mathrm{N{-}O_4}$	1.341 (4)	0.054	$\mathrm{O_2{\cdot\cdot\cdot}O_7}$	4.327 (38)	0.132 (28)
$\mathrm{O_6{\cdot}O_7}$	2.198 (36)	[0.048]	$\mathrm{N_5{\cdot\cdot\cdot}N_9}$	3.628 (50)	[0.25]
$\mathrm{O_4{\cdot}O_6}$	2.152 (10)	[0.048]	$\mathrm{O_6{\cdot\cdot\cdot}N_9}$	3.081 (106)	[0.25]
$\mathrm{O_4{\cdot}O_7}$	2.190 (41)	[0.048]	$\mathrm{O_7{\cdot\cdot\cdot}N_9}$	4.481 (83)	[0.30]
$\mathrm{O_2{\cdot}O_3}$	2.638 (54)	[0.080]	$\mathrm{O_6{\cdot\cdot\cdot\cdot}O_{10}}$	3.001 (186)	[0.30]
$\mathrm{Cr{\cdot}N}$	2.509 (7)	0.053 (6)	$\mathrm{O_3{\cdot\cdot\cdot}O_7}$	4.817 (40)	0.163 (25)
$\mathrm{O_2{\cdot}O_4}$	2.667 (4)	0.083 (24)	$\mathrm{O_4{\cdot\cdot\cdot}O_{11}}$	4.783 (72)	0.163
$\mathrm{O_2{\cdot}O_8}$	2.810 (18)	0.083	$\mathrm{O_6{\cdot\cdot\cdot\cdot}O_{11}}$	3.835 (106)	[0.25]
$\mathrm{O_4{\cdot}O_8}$	3.679 (40)	[0.100]	$\mathrm{O_7{\cdot\cdot\cdot\cdot}O_{11}}$	5.175 (155)	[0.30]
$\mathrm{Cr{\cdot\cdot}O_7}$	3.667 (8)	0.069 (6)	$\mathrm{O_4{\cdot\cdot\cdot}O_{10}}$	2.953 (39)	[0.20]

[a] Dihedral angle between the indicated planes. [b] Twist of the $\mathrm{O{=}Cr{=}O}$ group around the C_2 axis; see text.

shoulder at 1.9 Å may be assigned to these bonds. Other important terms are $\mathrm{O_N{\cdot}O_N}$, $\mathrm{O_{Cr}{\cdot}O_{Cr}}$, and Cr·N, occurring respectively at about 2.15, 2.25, and 2.50 Å, and the strong peak at 3.7 Å to which may be assigned Cr·O distances across two bond angles and other torsion-sensitive terms; that this last peak is quite sharp suggests the molecule is not a floppy one. Interpretations of the remaining features of the RD curve were not obvious, but those cited above provided a good basis for building trial structures for further testing.

Models and Refinements. Several models of the molecule differing in coordination mode of the nitrate groups about Cr were tested. Only one model, that depicted in Figure 3, was found that gave a satisfactory fit to the experimental RD curve. This model, which has C_2 symmetry, is based on octahedral coordination of the chromium atom, with the Cr bonding consisting of two multiple bonds to individual oxygen atoms, two single bonds to bridging oxygens in the nitrate groups, and two very weak bonds to peripheral oxygens in the nitrate groups; the angle between the planes $\mathrm{O{=}Cr{=}O}$ and $\mathrm{O{-}Cr{-}O}$ is close to 90°. The N—O (bridging) bonds roughly stagger the $\mathrm{Cr{=}O}$ and $\mathrm{Cr{-}O}$ bonds, and the $\mathrm{CrONO_2}$ units are close to planar. This model is certainly unusual in respect to the coordination about the Cr atom. We are aware of the tendency of chromyl halides to form small amounts of dimers in the gas[21] and from our own work the tendency in the solid for the ligands in chromyl compounds to act as bidentate ligands. Although a dimeric version of the $\mathrm{CrO_2(NO_3)_2}$ structure with a more conventional coordination number for the Cr atom can be devised, there seemed no reason to consider it: The high volatility of our sample is consistent only with a monomer, and the tendency for dimerization in the gas is surely small.

Given C_2 symmetry for the molecule, 13 geometrical parameters are required to define the structure. Convenient parameters are the distances $r(\mathrm{Cr{=}O})$, $r(\mathrm{Cr{-}O})$, $r(\mathrm{O{-}N})$, $\langle r(\mathrm{N{=}O})\rangle = {}^1/_2[r(\mathrm{N{=}O_6}) + r(\mathrm{N{=}O_7})]$, and $\Delta(\mathrm{N{=}O}) = {}^1/_2[r(\mathrm{N{=}O_6}) - r(\mathrm{N{=}O_7})]$; the angles $\angle(\mathrm{O{=}Cr{=}O})$, $\angle(\mathrm{O{-}Cr{-}O})$, $\angle(\mathrm{Cr{-}O{-}N})$, $\langle\angle(\mathrm{O{-}N{=}O})\rangle = {}^1/_2[\angle(\mathrm{O{-}N{=}O_6}) + \angle(\mathrm{O{-}N{=}O_7})]$, and $\Delta\angle(\mathrm{O{-}N{=}O}) = {}^1/_2[\angle(\mathrm{O{-}N{=}O_6}) - \angle(\mathrm{O{-}N{=}O_7})]$; and the torsions $\tau(\mathrm{Cr{-}O})$, $\tau(\mathrm{O{-}N})$, and $\tau(\mathrm{CrO_2})$. The torsions $\tau(\mathrm{Cr{-}O})$ and $\tau(\mathrm{O{-}N})$ define rotation about the designated bonds. When $\tau(\mathrm{Cr{-}O}) = 0$, the chain of single bonds $\mathrm{N{-}O{-}Cr{-}O{-}N}$ is planar trans–trans; positive values of $\tau(\mathrm{Cr{-}O})$ corresponds to clockwise rotation of the N—O bond looking from O to Cr along the Cr—O bond. If $\tau(\mathrm{O{-}N}) = 0$, the chain $\mathrm{Cr{-}O{-}N{=}O}$ is planar trans, and positive values of $\tau(\mathrm{O{-}N})$ indicate anticlockwise rotation of the $\mathrm{N{=}O}$ bond looking from N to O along N—O. $\tau(\mathrm{CrO_2})$ describes rotation of the $\mathrm{O{=}Cr{=}O}$ plane about the C_2 axis; a zero value for this parameter corresponds to a dihedral angle of 90° for the planes $\mathrm{O{=}Cr{=}O}$ and $\mathrm{O{-}Cr{-}O}$. Planarity of the nitrate groups was imposed throughout the structure determination, because it was clear that small deviations from planarity in $\mathrm{CrO_2(NO_3)_2}$ could not be detected from the electron-diffraction data and because no deviations have been established in the many nitrate structures considered in the review article[9] mentioned earlier. Constraints were imposed on those of the many amplitude parameters that could not be refined independently. Some were held at reasonable values estimated from those found in similar molecules such as $\mathrm{CrO_2Cl_2}$[4] or $\mathrm{N_2O_5}$.[22] In other cases groups were formed and each refined as a single parameter. For example, the differences between $l(\mathrm{N{=}O_6})$ and $l(\mathrm{O{-}N})$, and between $l(\mathrm{N{=}O_6})$ and $l(\mathrm{N{=}O_7})$, were fixed at values estimated from the variation in force constant with distance predicted by Badger's rules.[23] In still other cases, for example $l(\mathrm{O_3{\cdot\cdot}N_5})$ and $l(\mathrm{O_4{\cdot\cdot}N_9})$, and $l(\mathrm{O_3{\cdot\cdot}O_7})$ and $l(\mathrm{O_4{\cdot\cdot}O_{11}})$, the

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(20) There is considerable uncertainty about the covalent radius of Cr in this case. The upper limit is obtained from Pauling's ennea value (Pauling, L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 746) combined with his F radius (see ref 22). The lower limit is from his ennea value for Cr and the Schomaker–Stevenson F radius (Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37) with correction for electronegativity.

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Table II. Correlation Matrix (×100) for $CrO_2(NO_3)_2$

no.	param	σ_{LS}[a]	r_1	r_2	r_3	$\langle r_4 \rangle$	Δr_5	$\angle_6$	$\angle_7$	$\angle_8$	$\langle \angle_9 \rangle$	$\Delta\angle_{10}$	τ_{11}	τ_{12}	τ_{13}
							Geometrical Parameters[b]								
1	r(C=O)	0.051	100	7	-5	13	-12	4	5	<1	-13	15	5	-5	7
2	r(Cr—O)	0.16		100	-14	7	-5	42	4	-30	4	14	26	36	32
3	r(O—N)	0.14			100	34	-5	-24	-22	-8	-57	47	-40	-33	-39
4	$\langle r$(N=O)$\rangle$	0.058				100	-17	-15	-2	-10	-70	69	-15	-45	-21
5	Δr(N=O)	0.12					100	-5	-8	15	38	-46	-9	18	-12
6	∠(O=Cr=O)	124.4						100	13	6	21	-11	31	50	66
7	∠(O—Cr—O)	117.4							100	-70	-9	10	83	-10	32
8	∠(Cr—O—N)	11.7								100	20	-25	-53	19	-23
9	⟨∠(O=N—O)⟩	64.2									100	-96	16	60	21
10	Δ∠(O=N—O)	79.2										100	-9	-58	-10
11	τ(Cr—O)	139.7											100	16	47
12	τ(O—N)	99.0												100	35
13	$\tau(CrO_2)$	38.6													100
							Amplitude Parameters[c]								
14	l(Cr=O)	0.072	-8	-6	27	-3	35	-3	-34	31	12	-19	-32	22	-26
15	l(Cr—O)	0.143	-7	8	42	25	14	3	-45	-2	2	-37	10	-22	42
16	l(N=O)	0.171	<1	2	27	-76	6	-14	13	-30	35	-11	-4	<1	-12
17	l(Cr·N)	0.202	-8	-42	38	16	16	-51	-17	15	-12	-3	-31	-25	-71
18	$l(O_2 \cdot O_4)$	0.825	-2	-24	20	9	14	-15	11	5	-7	-3	2	-21	-61
19	$l(Cr \cdot\cdot O_6)$	0.568	1	7	47	26	11	4	-71	44	-4	3	-64	13	-29
20	$l(Cr \cdot\cdot O_7)$	0.172	-1	-8	16	5	1	6	-24	19	-5	2	-20	9	-4
21	$l(O_2 \cdot\cdot N_5)$	1.564	-2	-3	4	-2	2	19	34	-19	-9	4	10	16	9
22	$l(O_3 \cdot\cdot N_5)$	0.859	4	3	-22	-5	-8	-12	40	-18	20	-16	53	-12	-7
23	$l(O_2 \cdot\cdot O_7)$	0.961	-1	-8	<1	<1	2	-3	4	-1	3	-3	9	-2	-3
24	$l(O_3 \cdot\cdot O_7)$	0.848	3	1	11	12	-7	14	6	-4	-19	18	-10	-8	7

[a] Values for distances (r) and amplitudes (l) in angstroms; values for angles (∠, τ) in degrees. [b] For definitions, see text. [c] Only correlations with geometrical parameters are given.

groupings were made on the basis of a similar variation of corresponding distances with twist angle. The amplitude assumptions are evident from Table I.

Early least-squares refinements tended to give similar values for parameters insensitive to torsion. The problem of the long-range structure of the molecule, i.e., measurement of the parameters τ(Cr—O), τ(O—N), and $\tau(CrO_2)$, was simplified by this fact combined with expectation that the values of $\tau(CrO_2)$ and τ(O—N) were close to zero: A zero value for $\tau(CrO_2)$ corresponds to C_{2v} symmetry for the strong bonds about the Cr atom, as is found in the chromyl halides. A zero value for τ(O—N) corresponds to planarity of the O_2NOCr group similar to that for the O_2NOX grouping found in nitrates such as HNO_3, FNO_3, $ClNO_3$, and H_3CNO_3—a conformational preference, incidentally, that has been rationalized in terms of the variation of one-electron core orbital energies with geometry.[24] Further simplification of the problem arose when it became evident that under these conditions all but a small range of values for the parameter τ(Cr—O) were precluded by nonbonded O·O contacts of less than 2.60 Å. Additional refinements were then started from different values of τ(Cr—O) in the allowed range of this parameter, for models otherwise defined by τ(O—N) = 0, and by values of distances and bond angles similar to those in Table I. Only one minimum was found—one that corresponded, moreover, to a good fit to the data. In the final refinements the parameters τ(Cr—O) and $\tau(CrO_2)$ were released, the first because the local environment about the nitrogen atoms in $CrO_2(NO_3)_2$ is not symmetrical and therefore planarity of the $Cr—ONO_2$ group might not be maintained, and the second to remove the C_{2v} symmetry restriction on the strong bonds to Cr. Results for the final model are given in Table I, and a correlation matrix for the parameters is given in Table II.

Theoretical Structure. Since elucidation of the structure of gaseous $CrO_2(NO_3)_2$ tests the limit of the electron-diffraction technique, we decided to check the experimental conclusions by carrying out theoretical calculations. It is well-known that the molecular structures of typical organic and main-group inorganic compounds can be predicted with impressive reliability.[25] Experience with transition-metal derivatives is much less extensive, and though SCF methods are encouraging,[26] they fail badly in some cases (e.g. ferrocene[27] and iron pentacarbonyl[28]).

Table III. Ab Initio Results for Geometry Optimization of $CrO_2(NO_3)_2$[a]

optimized params		calcd distances and angles	
item	r/Å; ∠, τ/deg	item	r/Å; ∠/deg
r_e(Cr=O)	1.522	$r_e(N{=}O_6)$	1.302
r_e(Cr—O)	1.958	$r_e(N{=}O_7)$	1.187
r_e(O—N)	1.342	r_e(Cr·N)	2.540
$\langle r_e$(N=O)$\rangle$	1.205	r_e(Cr←O)	2.191
Δr_e(N=O)	0.057	$r_e(Ce \cdot\cdot O_7)$	3.721
$\angle_e$(O=Cr=O)	105.0	$\angle_e(O_2{=}Cr—O_4)$	105.5
$\angle_e$(O—Cr—O)	146.9	$\angle_e(O—N{=}O_6)$	109.2
$\angle_e$(Cr—O—N)	99.0	$\angle_e(O—N{=}O_7)$	123.5
$\langle\angle_e$(O=N—O)$\rangle$	116.3	$\angle_e$(O=N=O)	127.4
$\Delta\angle_e$(O=N—O)	-7.1		
τ_e(Cr—O)	140.1		
τ_e(O—N)	0.8		
$\tau_e(CrO_2)$[b]	7.1		

[a] For description of parameters and basis set, see text. [b] Twist of the O=Cr=O group around the C_2 axis; see text.

Geometry optimizations were carried out with the program Gaussian 90[29] installed on a Cray Y/MP 216 computer in Melbourne, Austrialia. C_2 symmetry for the molecule was assumed. In the initial work we used the double-ζ "Los Alamos" pseudopotential basis for Cr[30] and valence double-ζ bases for N

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and O,[31] which totaled 108 contracted functions from 284 primitives. Each cycle of gradient optimization required about 1200 CPU·s. Unfortunately, this level of theory gave r(C═O) = 1.403 Å, an unreasonably small value by any standard. (A subsequent, essentially similar calculation for the much simpler molecule CrO_2F_2, where r_g(Cr═O) was measured to be 1.575 (2) Å,[3] led to the value 1.413 Å.) We then turned to an all-electron basis for Cr. Wachters's 14s9p primitives[32] were contracted to 8s5p, an extra p function (exponent 0.14 chosen by downward extrapolation) was added to improve the description of any 4p-type electron density, and the 5d primitives of Rappe et al.[33] were adopted in a 41 contraction. Dunning's 4s2p contraction[34] of Huzinaga's 9s5p primitives[35] was used for N and O. A basis of this type has been shown to yield a reasonably accurate geometry for CrO_2F_2 at the SCF level.[36] Despite the substantial increase in size of this basis (136 contracted functions, 309 primitives), very little additonal CPU time per optimization cycle was required. The final results are found in Table III. It is seen that the optimized parameter values agree well with those derived from the experiment.

Discussion

Our model of the $CrO_2(NO_3)_2$ structure is a simple one—that of a single-conformer, semirigid molecule. In view of the large amplitude motion observed in the much less complex structure of N_2O_5,[22] the success of this model was unexpected and is clearly indicative of stabilizing interactions between peripheral oxygen atoms of the nitrate groups and other parts of the molecule.

The coordination of Cr in $CrO_2(NO_3)_2$ (Figure 3) is unusual, if not unique, for a chromium-containing molecule: the metal is linked to six O atoms (symmetry related in pairs) in a severely distorted octahedral arrangement. The three bond types are very different. One, Cr—O_4, with a length of 1.955 Å, may be regarded as a near-single bond since it lies just outside the range 1.81–1.92 Å cited earlier for this bond type; it will henceforth be symbolized as Cr—O. The Cr—O_2 distance of 1.586 Å is thus a multiple bond of order somewhat greater than two, and for simplicity we represent it by Cr═O. The Cr·O_6 distance (hereafter Cr←O) at 2.24 Å has a bond order about 0.19–0.29 according to Pauling's bond-order–bond-length formula[37] and should thus be characterized as a very weak bond. The distorted octahedral arrangement of the ligand atoms may be visualized in terms of a near plane that contains the four bonds of types Cr═O and Cr·O (the dihedral of the O═Cr═O and O·Cr·O planes is about 17°). Atoms O_4 and O_8 are positioned roughly above and below the center of this approximate plane.

Designation of Cr·O as a "bond" deserves comment. Although much longer than a nominal Cr—O single bond, Cr←O is also very much shorter than the van der Waals Cr···O distance of about 3.4–3.5 Å estimated by adding 0.80 Å to each of the covalent radii. In the absence of bonding, such a short distance would imply strong repulsion between Cr and O_6, which could be largely relieved either by torsion around the N—O_{Cr} bond (parameter τ(O—N)) or a rock of the $-NO_2$ group so as to move O_6 away from Cr. Instead, the experimental value of τ(O—N) corresponds to near planarity of the Cr—O—NO_2 group and the $-NO_2$ group is rocked toward Cr by a few degrees. Besides the difference ∠O—N═O_6 − ∠O—N═O_7 = −7° representing the rock just mentioned, evidence of an attractive interaction between O_6 and Cr is also to be seen in the N—O distances of the nitrate group and in the Cr—O—N angle. Formation of bonds of the type Cr·O_6 should lead to a weakening, and hence a lengthening, of N═O_6 relative to N═O_7; such a lengthening of about 0.06 Å is observed. The bridging Cr—O—N angle at 97.5 (5)° is significantly smaller than that in N_2O_5 (111.8 (16)°),[22] where attractive forces across the bridging oxygen do not exist. It is worth noting that the nitrate groups in $CrO_2(NO_3)_2$ are substantially less asymmetrical than in typical covalent nitrates. The difference between the bridging and average terminal nitrogen–oxygen distances in our compound is only 0.12 Å, whereas it is 0.31 Å in N_2O_5, 0.19 Å in CH_3NO_3,[38] and 0.20 Å in HNO_3.[39] Also, our values for ∠O═N═O and (average) ∠O—N═O differ by only 13°, but in this difference is 20° N_2O_5, 14° in CH_3ONO_2, and 15° in $HONO_2$. The implication is that in $CrO_2(NO_3)_2$ the Cr·O bonds have considerable ionic character.

Chromyl compounds with 4-fold coordination of the metal, such as $CrO_2(OCPh_3)_2$[40] and the halides,[3,4] have O═Cr═O groups with similar structures. Interestingly, the structure of this group in $CrO_2(NO_3)_2$ with 6-fold metal coordination is similar to that in the tetrahedral compounds, and accommodation of the extra pair of O's in the coordination spehere of Cr is achieved largely by an opening of the O—Cr—O bond angle. Thus, relative to the angle values ∠O—Cr—O = 110.04 (9)° and ∠O═Cr—O = 106.94 (9)° and 111.58 (9)° in $CrO_2(OCPh_3)_2$, in $CrO_2(NO_3)_2$ the O—Cr—O angle has been opened up some 30° and the O═Cr—O angle correspondingly decreased about 6° to make room for the additional pair of Cr←O bonds at an angle O→Cr←O equal to 85°. These Cr←O bonds serve to anchor the $-NO_2$ groups: whereas in N_2O_5 these groups are subject to large amplitude torsional motion, in $CrO_2(NO_3)_2$ the modest amplitude values for the torsion-sensitive distances indicate that the molecule is rather stiff.

Vibrational stretching frequencies for N–O bonds have been found to correlate satisfactorily with the bond lengths.[41] The vibrational spectrum of $CrO_2(NO_3)_2$ has been partially recorded but not assigned in any detail.[18] From this frequency–bond-length relationship the highest frequency band seen at 1625–1675 cm^{-1} implies a bond length of 1.19 Å, and the next highest, an intense band band at 1300–1350 cm^{-1}, a bond length of 1.25 Å. The agreement of these predicted values with our measured ones r(N═O_7) = 1.193 (4) Å and r(N═O_6) = 1.254 (4) Å is astonishingly good. Our value r(N═O) = 1.342 (4) Å implies a stretching frequency of about 930 cm^{-1}; there is indeed a peak in the IR spectrum of $CrO_2(NO_3)_2$ at 940–970 cm^{-1}, but this may well be due, at least in part, to the Cr═O stretching motions which are typically found near 1000 cm^{-1}. It should also be acknowledged that an additional strong band at 1203–1235 cm^{-1} does not fit straightforwardly into the pattern expected on the basis of our structural results and the relationship between bond length and stretching frequency; this discrepancy may be due to vibrational coupling between the two nitrate groups in $CrO_2(NO_3)_2$.

It is gratifying that the SCF results (Table III) agree in most major respects with those deduced from the electron-diffraction experiment. Among these are the irregular octahedral coordination about the Cr atom, the values of r(Cr—O, r(Cr←O), and ∠(O—Cr—O), and the differences in the N═O bond lengths and the bond angles about the N atoms. It is particularly pleasing that the calculations indicate a twisting distortion away from local C_{2v} symmetry about the Cr atom comparable to the experimental result, and that the calculated nonplanarity of the -O—NO_2 group (0.1°) justifies the assumption of planarity made in the experimental analysis. Less pleasing is the calculated value for r(C═O), which is 0.062 Å shorter than the experimental one. Since a similar difference (0.060 Å) was found in the case of CrO_2F_2 where the structure is well-known, we attribute the error to deficiencies in the SCF approximation. Differences between theory and experiment for the angles around the N atom are probably due to

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the limited size of the basis set: it is well-known that unpolarized double-ζ bases give poorer values for bond angles at atoms with lone pairs than they do for bond lengths.[25] Last, we note the poor value for r(C=O) obtained by use of the pseudopotential for Cr instead of the all-electron model. This result, and the similar one obtained for CrO_2F_2, indicates the pseudopotential may have insufficient flexibility to describe the Cr atom core in highly positive environments created by the presence of very electronegative substituents.

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Supplementary Material Available: Tables of total intensities and final backgrounds from each plate and average intensities (9 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of British Columbia,
Vancouver, British Columbia, Canada V6T 1Z1, and Northwestern University, Evanston, Illinois 60208-3113

Synthesis and Characterization of Dihalogenoruthenium(IV)-, Diphenylruthenium(IV)-, and Phenylruthenium(III)-Tetraphenylporphyrin Complexes, Including the Crystal Structure of $Ru(TPP)Br_2$

Mingzhe Ke,[1a] Chand Sishta,[1a] Brian R. James,*[,1a] David Dolphin,[1a] John W. Sparapany,[1b] and James A. Ibers*[,1b]

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The paramagnetic ($S = 1$) $Ru(TPP)X_2$ complexes (X = halide) are made by treatment of $[Ru(TPP)]_2$ with HBr, HCl, or I_2 (TPP = the dianion of 5,10,15,20-tetraphenylporphyrin). The dibromo species (**2**) crystallizes in the tetragonal system, space group C_{4h}^5-$I4/m$, with $a = 13.686$ (9) Å, $c = 9.711$ (7) Å, and $Z = 2$. The structure has been refined on F^2 to final R and R_w values of 0.050 and 0.080, respectively, for 72 variables and 1639 observations; the value of $R(F)$ for the 1354 reflections having $F_o^2 \geq 3\sigma(F_o^2)$ is 0.034. The molecule has imposed symmetry $4/m$. As a consequence, the porphyrin plane is strictly planar; the phenyl rings are perpendicular to this plane, as is the Ru-Br bond. The Ru-Br distance is 2.425 (2) Å, the shortest recorded for any Ru-Br bond. ^{1}H NMR isotropic shift data are consistent with π-donation from the halide. With PhLi, **2** yields diamagnetic $Ru(TPP)Ph_2$ (**5**), which can be thermally decomposed to Ru(TPP)Ph (**6**); kinetic data imply a stronger Ru-C bond in **5** compared to the corresponding octaethylporphyrin complex (by 2.6 kcal/mol). A light-induced O_2 oxidation of **6** gives diamagnetic $[Ru(TPP)Ph]_2O$.

Introduction

Organometallic chemistry at metalloporphyrin centers is of current interest, and developments in such chemistry of ruthenium porphyrins (excluding the carbonyl complexes) originally stemmed, at least in part, from attempts to model certain aspects of cytochrome P450 systems where Fe-carbon and porphyrin nitrogen-carbon bonded intermediates are implied.[2] Work from this laboratory first reported an entry into Ru(porphyrin)(π-olefin) complexes,[3] and such chemistry involving direct coordination of an olefin (or acetylene) at a Ru(II) porphyrin center has been extended by ourselves,[4] and others.[5,6] A more extensive organoruthenium porphyrin chemistry with derivatives in oxidation states II-IV has been developed via reactions of electrophiles with Ru(0) precursors[5,7] or via treatment of Ru(IV) dihalides or dimeric $[Ru(por)]_2^{2+}$ precursors with Grignard reagents or lithium alkyls/aryls.[2,8-10] Synthesized $Ru(por)R_2$ and Ru(por)R species (R = aryl, alkyl) themselves have extensive redox chemistry[2,9,11] that enriches further this organometallic area.

The porphyrin ligands utilized in the above reports have been mainly OEP[2,3,7-9,11] and TTP[5,7] and occasionally TMP[4,6] and OCP.[6] The present paper reports on TPP derivatives, in particular the $Ru(TPP)X_2$ complexes where X = Cl, Br, and I (including a structure of the X = Br species), $Ru(TPP)Ph_2$, and Ru(TPP)Ph; in an earlier communication,[11] we noted the existence of such complexes and listed the ^{1}H NMR data for Ru(TPP)Ph.

Experimental Section

^{1}H NMR spectra were obtained on a Varian XL 300-MHz or Bruker WH 400-MHz FT spectrometer. UV/visible spectra were recorded on a Perkin-Elmer 552A spectrophotometer, and mass spectra (EI and FAB) were obtained on a Kratos-AEI MS902 instrument; FAB spectra in a p-nitrobenzyl alcohol matrix were acquired with a 6-kV ion source, a 7-8-kV, 1-mA xenon gun, and a 10 s/decade scan rate. Elemental analyses were carried out by P. Borda of the Department of Chemistry, UBC. Solution magnetic moment measurements at room temperature were done by the Evans method, using 5-10 mM concentrations of the complexes in $CDCl_3$ with TMS as reference (2% in volume);[12] diamagnetic corrections were made by totaling individual contributions from each atom present with the use of Pascal's constants.[13]

Anhydrous HBr(g) was obtained from Matheson, and technical grade HCl(g) was supplied by BDH Chemical Co; O_2 was obtained from Union Carbide of Canada Ltd. and dried where necessary by passage through an Aquasorb tube (Mallinckrodt); I_2 and PhLi (2.0 M in cyclohexane/diethyl ether, 70/30) were Aldrich products; solvents except benzene and toluene were used directly without further purification; benzene and toluene were refluxed and distilled from CaH_2 and stored over molecular sieves (4 Å) under N_2. Where necessary, the solvent was degassed by three to six freeze-pump-thaw cycles. Ru was obtained on loan from Johnson Matthey Ltd., in the form of $RuCl_3 \cdot H_2O$ (~40% Ru). The

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(10) Abbreviations used: por = dianion of an unspecified porphyrin; OEP = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; TTP, TMP, OCP, and TPP are dianions of the 5,10,15,20-tetrasubstituted porphyrins with p-tolyl, mesityl, 2,6-dichlorophenyl, and phenyl groups, respectively; py = pyridine; Cp = η^5-cyclopentadienyl; in NMR spectra, s = singlet, d = doublet, t = triplet, and b = broad; in UV/vis spectra, sh = shoulder.

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