and −525 ppm.[12] The metal–metal interactions in these related molecules might be similar.

For this class of dinuclear compound, the [195]Pt NMR data is most diagnostic of this structural type. However, the rather large $^1J_{PtP}$ and $^2J_{PtP}$ couplings to P^a are also diagnostically important parameters that are readily evident in the ^{31}P NMR spectra.

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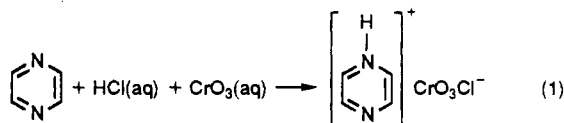and Washington State University,
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Crystal Structure of Pyrazinium Chlorochromate

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The preparation, reactions, and structures of high-valent chromium(VI) complexes continue to attract the attention of chemists who are interested in their ability to function as effective and selective oxidants. In previous studies, we and others have found chromium(VI) heterocyclic complexes to be effective and selective oxidants with a number of primary and secondary alcohols.[1–5] In two recent reports, a bond length correlation for $(Cr_nO_{3n+1})^{2-}$ anions was presented[6] and the existence of some short C–H⋯O contacts between the dichromate ion and a cation were observed.[7]

In our attempts to study effective and selective organic oxidants, pyrazinium chlorochromate was prepared via the reaction[4]

$$\left[\begin{array}{c} N \\ \boxed{} \\ N \end{array} \right] + HCl(aq) + CrO_3(aq) \longrightarrow \left[\begin{array}{c} H \\ | \\ N \\ \boxed{} \\ N \end{array} \right]^+ CrO_3Cl^- \qquad (1)$$

A stable nonhygroscopic solid, with a shelf life of at least 3 months when stored in the dark,[4] pyrazinium chlorochromate was found to be an efficient but mild oxidant for a number of alcohols.[4] Spectroscopic and solubility characteristics were supportive[4] of an ionic structure. This note reports the results of a single-crystal X-ray structural analysis. A further exploration of short C–H⋯O interactions in chromate salts with organic cations will be given.

Experimental Section

The pyrazinium chlorochromate crystals were prepared according to the literature method.[4] An irregularly shaped orange crystal, 0.30 × 0.60 × 0.15 mm, was mounted on a Syntex P2₁ diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å), upgraded to Nicolet P3F specifications. Cell constants were defined by a least-squares refinement from 24 reflections in the range $31° < 2\theta < 40°$.[8] A total of 749 reflections were measured by ω scans ($3 \leq 2\theta \leq 70°$, $((\sin \theta)/\lambda)_{max}$ = 0.807 Å, $0 \leq h \leq 18, 0 \leq k \leq 9, 0 \leq l \leq 7$), with 749 unique and 712 observed ($F \geq 3\sigma(F)$) reflections. Empirical (ψ-scan) absorption corrections assuming an ellipsoidal crystal and Lorentz and polarization corrections were made.

Structure solution programs were obtained from the SHELXTL package.[9] Scattering factors were obtained from ref 10. Systematic ab-

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formula: $C_4H_4N_2HCrO_3Cl$	T = 22 °C
	λ = 0.71069 Å
a = 11.615 (3) Å	ρ_{calcd} = 1.93 g cm⁻³
b = 5.658 (1) Å	μ = 18.2 cm⁻¹
c = 5.657 (2) Å	transm coeff = 0.724–0.940
V = 371.7 Å³	$R(F_o)$ = 0.022 (= 0.024, for all reflcns)
Z = 2	$R_w(F_o)$ = 0.030 (= 0.030, for all reflcns)
fw = 216.3	
space group: *Pma*2 (No. 28)	

Table II. Non-Hydrogen Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (10³ × Å²) for $C_4H_4N_2HCrO_3Cl$

atom	x	y	z	$U_{iso}{}^a$
Cr	7500	−2157 (1)	0	21 (1)
Cl	7500	−1798 (2)	−3856 (2)	34 (1)
O(1)	6345 (2)	−876 (4)	919 (4)	36 (1)
O(2)	7500	−4918 (4)	661 (5)	34 (1)
N(1)	5000	5000	8031 (7)	25 (1)
N(2)	5000	5000	3188 (7)	29 (1)
C(1)	5536 (2)	3316 (4)	6800 (4)	28 (1)
C(2)	5549 (2)	3290 (4)	4347 (4)	29 (1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Non-Hydrogen Interatomic Distances (Å) and Angles (deg) for $C_4H_4N_2HCrO_3Cl$

Distances			
Cr–O(1)	1.611 (2)	C(1)–C(2)	1.387 (4)
Cr–O(2)	1.606 (2)	N(1)–N(2c)^c	2.918
Cr–Cl	2.191 (1)	C(2)–O(1)	3.189
N(1)–C(1)	1.335 (3)	C(2)–O(1d)^d	3.235
N(2)–C(2)	1.332 (3)	C(2)–O(2e)^e	3.242

Angles			
O(1)–Cr–O(2)	111.2 (1)	C(1)–N(1)–C(1b)^b	117.0 (4)
O(1)–Cr–Cl	106.2 (1)	C(2)–N(2)–C(2b)^b	121.0 (4)
O(2)–Cr–Cl	108.8 (1)	N(1)–C(1)–C(2)	112.3 (2)
O(1)–Cr–O(1a)^a	112.8 (1)	N(2)–C(2)–C(1)	118.7 (2)

^{a} Denotes atom whose coordinates were transformed by $1.5 - x, y, z$.
^{b} Denotes atom whose coordinates were transformed by $1 - x, 1 - y, z$.
^{c} Denotes atom whose coordinates were transformed by $x, y, 1 + z$.
^{d} Denotes atom whose coordinates were transformed by $1 - x, -y, z$.
^{e} Denotes atom whose coordinates were transformed by $x, 1 + y, z$.

sences ($h0l$, h odd) indicate *Pma*2, *Pmam*, and $P2_1am$ as possible space groups. Since the centrosymmetric alternative (*Pmam*) requires the chromium atom to be at a site of C_{2v} or C_{2h} symmetry, an impossible situation since the anion has no 2-fold axis, only the two noncentrosymmetric alternatives were considered. All atom positions, including H atoms, were identified from direct methods and subsequent electron density difference maps when the space group *Pma*2 was tried. Final refinement of 56 least-squares parameters gave the $R(F_o)$ values listed in Table I. The left-hand alternative for the coordinate system was rejected on the basis of a higher $R_w(F_o)$ = 0.033 for the 3σ data set. Excursions in the final electron density difference map ranged from −0.3 to +0.3 e/Å³ (near Cl). The two possible alternatives of interchanging carbon with nitrogen atoms in the ring were rejected on the basis of higher $R_w(F_o)$; $R_w(F_o)$ = 0.053 and $R_w(F_o)$ = 0.052, respectively, for the

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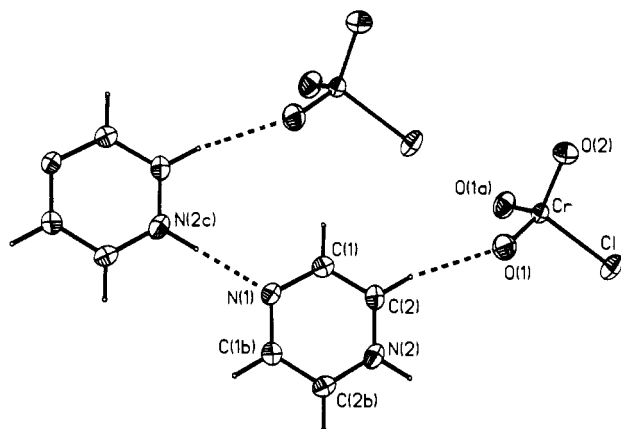
Figure 1. Thermal ellipsoid view of two formula units of $C_4H_4N_2HCrO_3Cl$ at 50% probability. Hydrogen atom positions are indicated by small spheres. Hydrogen bonds are indicated by dashed lines.

3σ data set. Crystal data are presented in Table I while non-hydrogen atomic coordinates are presented in Table II and selected bond lengths and angles are given in Table III.

Results and Discussion

The structure of pyrazinium chlorochromate consists of segregated chains of cations and anions aligned parallel to the c axis. The chlorochromate anion lies athwart a mirror plane that passes through Cr, Cl, and O(2) (see Figure 1). The planar cation lies on a 2-fold axis running through the nitrogen atoms. The cations are linked together into polar chains parallel to the c axis, through N(1)–H···H(2) hydrogen bonds (N(1)–N(2) = 2.918 Å). The anions separate the chains, and are arranged with Cr–Cl bonds aligned parallel to the c axis, also in a polar sense. The closest anionic interaction is 3.277 Å between the O(1) atom and O(1) atoms of neighboring tetrahedra. A comparison of the C–N and C–C lengths (1.314 and 1.358 Å) in pyrazine[11] versus analogous lengths (1.332 (5) and 1.387 (4) Å) in the pyrazinium cation shows that protonation produces significant lengthening of all bonds.

The anions and cation chains are linked by the formation of an unusual hydrogen bond interaction between oxygen O(1) of the CrO_3Cl group and carbon C(2) of the neighboring pyrazinium cation. The C–H···O distance found of 3.189 Å, with a C–H···O angle of 162°, is long compared to normal interactions involving O–H or N–H groups (2.3–2.8 Å). It is comparable, however, to the value of 3.2 Å for the C–H···N interaction reported for $(HCN)_n$.[12] Two other C–H···O interactions of lengths less than 3.25 Å (3.234 and 3.242 Å) are observed, but both involve acute C–H···O angles of <99° and so are considered less significant.

Structural characteristics have been examined for C–H···O interactions in organic compounds.[13,14] Observed H···O distances increase from 2.045 Å for linear C–H···O bonds to 2.4 Å as that angle approached 90°. Perhaps the shortest known C–H···O interactions occur where the planarity of a conjugated π-bonding system, I, forces the attractive C–H···O interaction to be excep-
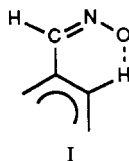
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tionally short.[15,16]   For organic compounds of the type $(Cl_{3-n}C_n)CH$, C···O distances down to the range 2.90–3.00 Å were
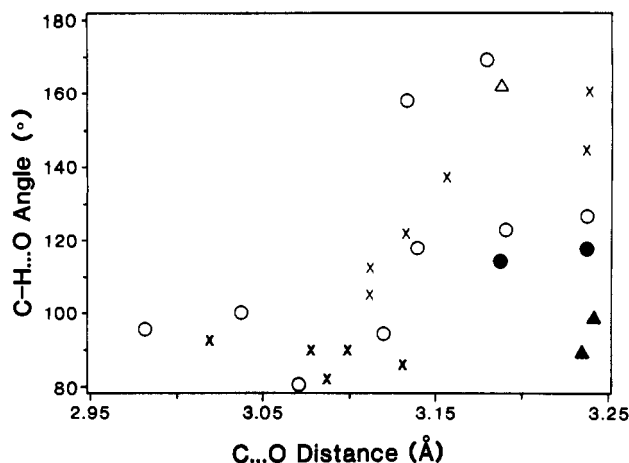
C...O Distance (Å)

Figure 2. Plot of observed C–H···O angles versus C···O distances: ($\triangle$) this work; (O) = pyrazinium N-oxide dichromate;[2] (×) pyrazinium trichromate.[1] Boldface or solid symbols denote interactions with $\omega \leq 50°$, C···O distances <3.25 Å, and C–H···O angles between 80 and 125°.

found for $Cl_3CH···O$ interactions, while the shortest CH···O distances were between 2.30 and 2.40 Å.[14] It was concluded that the C–H···O contact is primarily electrostatic in nature. The oxygen atoms in the CrO_3Cl^- anion certainly have a more negative charge than in organic compounds, and thus one can conclude that the observed C···O distance of 3.189 Å indeed represents a substantial electrostatic interaction.

Analysis of four organochromate structures located in the Cambridge Data Base[17] further supports this conclusion.[6,7,18,19] In Figure 2, the C–H···O angle is plotted versus the C···O distance. If we examine nearly linear C–H···O interactions (C–H···O angle $\geq 140°$), five contacts are found with distances less than 3.25 Å and thus represent linear hydrogen bond interactions.[1,2,11,12] Of these, only bis(pyrazinium N-oxide) dichromate[7] shows two C–H···O contacts (3.13 and 3.18 Å) approximately as short as that in pyrazinium chlorochromate.

Figure 2 contains further information that may clarify oxidation mechanisms of organic compounds by high-valent transition oxometalate complexes. In a postulated mechanism of oxidation of arylalkanes by CrO_2Cl_2,[20] the hydrocarbon initially binds to the oxidant by hydrogen bonding (C–H···O–Cr), followed by a rearrangement to bring the carbon atom into close juxtaposition to the chromium atom. The carbon–hydrogen bond is then cleaved, producing a chromium(IV) ester. Thus it is informative to note contacts in Figure 2 corresponding to the postulated hydrogen-bonded transition state. These contacts are highlighted in boldface and correspond to C–H···O angles in the range 85–125° with C–H···O–Cr torsional angles of $\omega \leq 50°$ where $\omega = 0°$ corresponds to the optimal configuration for minimizing Cr···C contacts. The significant number of found contacts shows the feasibility of such a reaction intermediate.

Supplementary Material Available: Figure SIII, showing a stereographic pair illustrating the unit cell, and Tables SIII–SV, containing a full listing of data collection and refinement parameters, the anisotropic thermal parameters, and derived hydrogen atom positions (4 pages); Table SVI, giving observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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