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Contribution from the Chemistry Department,
University of Houston, University Park, Houston, Texas 77004

Synthesis and Molecular Structure of Oxochromium(V) Cations. Coordination with Donor Ligands

K. Srinivasan and J. K. Kochi*

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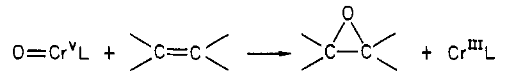
Synthesis of various oxochromium(V) cations ligated with salen [*N*,*N*′-ethylenebis(salicylideneaminato)], i.e. O=Cr(salen)$^+$, is readily achieved from the corresponding chromium(III) complex, (salen)Cr$^+$, by oxygen atom transfer with either iodosylbenzene or *m*-chloroperbenzoic acid. X-ray crystallographic analysis of O=Cr(salen)$^+$ indicates that the the 5-coordinate Cr atom is situated 0.53 Å above the salen (mean) plane and describes a square-pyramidal configuration with the oxo ligand occupying the apical position. Isotopic ^{18}O-substitution leads to a shift in the O=Cr stretching frequency from 1004 to 965 cm^{-1} in accord with theoretical predictions. Similarly the magnetic susceptibility and the well-resolved isotropic ESR spectra reliably reflect the d^1 electron configuration of the oxochromium(V) species in acetonitrile solutions. Oxochromium(V) and various donor ligands such as pyridine *N*-oxide, triphenylphosphine oxide, and water form 1:1 association complexes, the formation constants *K* of which vary from 10^{-2} to 10^3 M^{-1}, depending on the donor ligand and the substituent groups located on the salen periphery. X-ray crystallographic determination of the pyridine *N*-oxide adduct O=Cr(salen)(Opy)$^+$ indicates that the donor ligand fills the apical position in O=Cr(salen)$^+$ to complete the octahedral coordination about Cr. Isotopic ^{18}O-tracer studies of the formation of oxochromium(V) by oxygen atom transfer to the chromium(III) complex are described. From X-ray crystallography, the lattice parameters for the oxochromium(V) complex IIc are as follows: space group, $P2_1/n$, monoclinic; cell constants, a = 16.233 (2) Å, b = 6.439 (1) Å, c = 19.523 (4) Å, β = 94.44 (1)°, V = 2034.5 Å^3; Z = 4. The lattice parameters of the pyridine *N*-oxide adduct of the oxochromium(V) complex IIf are as follows: space group, $P4_32_12$, tetragonal; cell constants, a = 11.938 (1) Å, c = 43.366 (9) Å, V = 6174 Å^3; Z = 8.

Introduction

Chromium(V) species have been identified as transient intermediates during the reduction of various chromyl(VI) complexes.[1] Although a few reactive chromium(V) complexes are known, they have been mostly isolated as rather weak polymeric or anionic oxidants.[2] The presence of an oxo-chromium bond (i.e. O=Cr) is the most common feature of the metal in this high oxidation state. However, the chemistry associated with oxochromium(V) species is largely unexplored.

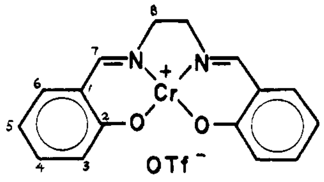
The possibility of effecting a direct transfer of an oxygen atom from the O=Cr functionality to a donor such as an olefin, e.g.



(1)

poses an interesting challenge, which has been recently realized with two series of chromium(V) complexes. Thus Groves and Kruper were the first to isolate a reactive red species characterized as the oxochromium(V) derivative of chloro(tetraphenylporphyrinato)chromium(III) by treatment with iodosylbenzene.[3] Subsequently we presented a series of active oxochromium(V) cations derived from various well-characterized [*N*,*N*′-ethylenebis(salicylidineaminato)]chromium(III) hexafluorophosphates by a similar procedure.[4] Although dark brown-black crystals of O=Cr(salen)PF$_6$ were of sufficient quality for a preliminary X-ray crystallographic determination, a minor crystalline disorder with the oxo–chromium sites caused us to investigate the problem further. In this report, we present a definitive crystal structure of the O=Cr(salen)$^+$ cation [salen = *N*,*N*′-ethylenebis(salicylideneaminato)], together with a complete spectroscopic characterization and a study of its coordination with various donor ligands in solution. The details of oxygen atom transfer from these unusual oxo derivatives of cationic salen–chromium complexes to olefinic substrates are reported separately.[5]

In order to resolve the crystallographic problem, we synthesized various analogues of the (salen)Cr^{III} salt by replacing the hexafluorophosphate counterion with trifluoromethanesulfonate (triflate = OTf) and placing substituents at various positions on the salen ligand. The various (salen)Cr^{III} complexes examined in this study are listed as Ia–g.[6]



I

a, unsubstituted
b, 5,5′-Cl_2
c, 7,7′-$(CH_3)_2$
d, 7,7′-$(C_6H_5)_2$
e, 8,8,8′,8′-$(CH_3)_4$
f, 5,5′-Cl_2-8,8,8′,8′-$(CH_3)_4$
g, 8,8′-*o*-C_6H_4

Experimental Section

Materials. Salicylaldehyde, 5-chlorosalicylaldehyde, *o*-hydroxyacetophenone, ethylenediamine and *o*-phenylenediamine from Fisher were used as received. *o*-Hydroxybenzophenone was synthesized by the Friedel–Crafts phenylation of *o*-hydroxybenzoyl chloride.[8] 2,3-Diamino-2,3-dimethylbutane was prepared from 2,3-dimethyl-2,3-dinitrobutane by acidic reduction with granular tin, followed by distillation from KOH pellets.[9] Iodosylbenzene was freshly prepared from iodobenzenediacetate (Aldrich), dried in vacuo and stored at −20 °C. Isotopically labeled ^{18}OIPh was prepared by the procedure described by Hill and Schardt.[10] Acetonitrile, acetone, methylene chloride, and chlorobenzene were reagent grade commercial solvents, which were repurified by standard methods[11] and redistilled prior to use. Trifluoromethanesulfonic (triflic) acid (3M Co.) was used as received.

The ligands salenH$_2$, salphenH$_2$, and 7,7′-Me$_2$salenH$_2$ were prepared by literature methods,[12] as were the 7,7′-diphenyl, 5,5′-dichloro, 8,8,8′8′-tetramethyl, and 5,5′-dichloro-8,8,8′,8′-tetramethyl analogues. They were recrystallized from ethanol as bright yellow solids, with the

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exception of 8,8,8′,8′-Me$_4$salenH$_2$, which was recrystallized from a 2:1 mixture of hexane and ether. Chromous triflate was prepared from electrolytic chromium chips (99.995% obtained from Varlacoid) by dissolution in 6 N aqueous triflic acid under rigorously anaerobic conditions.[13,14] It was obtained as a light blue solid by removal of the water in vacuo without exposure to air.

Instrumentation. The electronic absorption spectra were measured with a Hewlett-Packard 8450A diode-array spectrometer. The X-band ESR spectra were recorded on a Varian Centuryline E112 spectrometer equipped with an NMR gaussmeter for field frequency calibration. Magnetic susceptibility was measured at 25 °C by the Evans method[15] in acetonitrile solution by using a JEOL FX-90Q NMR spectrometer. Infrared spectra were obtained either on a Beckmann IR-8 (dispersion) or a Nicolet DX-10 (Fourier transform) spectrometer. Cyclic voltammetry was carried out on a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a Model 176 current-to-voltage converter, which provided a feedback compensation for ohmic drop between the working and reference electrodes. The voltammograms were recorded on a Houston Omnigraphic Series 2000 X-Y recorder. Organic analysis was carried out on a Hewlett-Packard Model 5890-5970 GC-MS utilizing a 20-ft silicone-coated capillary column.

General Procedure for the Synthesis of [*N*,*N*′-Ethylenebis(salicylideneaminato)]chromium(III) Triflates. A pure blue solution of chromous triflate in either anhydrous ethanol or acetone was added dropwise under an argon atmosphere to a suspension of slightly less than 1 equiv of the appropriate salen ligand in the same medium. The resulting dark brown solution was stirred for 30 min, exposed to air, and then heated to reflux for ~1 h. Removal of the solvent in vacuo afforded a wet yellow residue, which was stirred with water for 2 h. Separation by filtration, followed by three water washes, afforded a deep yellow product. The yield of each [*N*,*N*′-ethylenebis(salicylideneaminato)]chromium(III) triflate is separately reported below, together with the IR spectrum (Nujol mull), UV–vis spectrum (CH$_3$CN solution), and magnetic susceptibility.[16]

[(salen)Cr(H$_2$O)$_2$]O$_3$SCF$_3$ (Ia). Yield: 60%. IR (cm^{-1}): 3200–3500, 2800, 1640, 1620, 1535, 1300 (br), 1250, 1240, 1170, 1040 (br), 830, 720, 660. UV–vis [nm (ϵ (M^{-1} cm^{-1}))]: 418 (3118), 366 (4670) sh, 319 (9925) sh, 285 (1.7 × 10^4), 228 (4.8 × 10^4). μ_{eff}: 3.82 μ_B.

[(5,5′-Cl$_2$salen)Cr(H$_2$O)$_2$]O$_3$SCF$_3$ (I). Yield: 45%. IR (cm^{-1}): 3200–3500, 2800, 1650 (br), 1560, 1405, 1300, 1260 (br), 1240, 1170, 1140, 1040, 910, 760, 660. UV–vis [nm (ϵ (M^{-1} cm^{-1}))]: 428 (3741) 362 (7948) sh, 324 (1.14 × 10^4), 281 (2.05 × 10^4), 228 (6.29 × 10^4). μ_{eff}: 3.76 μ_B.

[(7,7′-Me$_2$salen)Cr(H$_2$O)$_2$]O$_3$SCF$_3$ (Ic). Yield: 49%. IR (cm^{-1}): 3200–3500, 2800, 1620, 1560, 1480, 1330, 1280 (br), 1170, 1040, 880, 750, 660. UV–vis [nm (ϵ (M^{-1} cm^{-1}))]: 414 (2750) (the usual shoulders at ~360 and 320 nm are not apparent), 277 (1.7 × 10^4), 228 (5.2 × 10^4). μ_{eff}: 3.55 μ_B.

[(7,7′-Ph$_2$salen)Cr(H$_2$O)$_2$]O$_3$SCF$_3$ (Id). Yield: 55%. IR (cm^{-1}): 3200–3500, 2800, 1620, 1610, 1560, 1480, 1340, 1320, 1310, 1240 (br), 1180, 1040, 860, 710, 660. UV–vis [nm (ϵ (M^{-1} cm^{-1}))]: 416 (4418), 360 (7433) sh, 317 (1.38 × 10^4) sh, 226 (4.5 × 10^4), 282 (1.51 × 10^4). μ_{eff}: 3.78 μ_B.

[(8,8,8′,8′-Me$_4$salen)Cr(H$_2$O)$_2$]O$_3$SCF$_3$ (Ie). Yield: 70%. IR (cm^{-1}): 3300–3600, 2800, 1625, 1610, 1550, 1470, 1300, 1290, 1240, 1220, 1170, 1140, 1120, 1030, 750, 650. UV–vis [nm (ϵ (M^{-1} cm^{-1}))]: 418 (4786), 360 (8112) sh, 316 (1.60 × 10^4) sh, 286 (2.5 × 10^4), 208 (6.8 × 10^4). μ_{eff}: 3.80 μ_B.

[(5,5′-Cl$_2$-8,8,8′,8′-Me$_4$salen)Cr(H$_2$O)$_2$]O$_3$SCF$_3$ (If). Yield: 75%. IR (cm^{-1}): 3300–3500, 2800, 1696, 1624, 1537, 1388, 1296, 1292, 1168, 1146, 1130, 1029, 822, 809, 706, 636. UV–vis [nm (ϵ (M^{-1} cm^{-1}))]: 432 (2970), 329 (8510), 284 (1.55 × 10^4), 262 (1.94 × 10^4), 228 (5.10 × 10^4).

[(8,8′-*o*-benzosalen or salphen)Cr(H$_2$O)$_2$]O$_3$SCF$_3$ (Ig). Yield: 45%. IR (cm^{-1}): 3300–3500, 2850, 1610, 1584, 1541, 1466, 1388, 1285, 1236, 1189, 1154, 1030, 926 (vw), 813, 740, 639. UV–vis [nm (ϵ (M^{-1} cm^{-1}))]: 476 (6210), 342 (1.94 × 10^4), 296 (1.88 × 10^4), 241 (2.69 × 10^4), 213 (4.13 × 10^4).

General Procedure for the Synthesis of [*N*,*N*′-Ethylenebis(salicylideneaminato)]oxochromium(V) Triflates. A slight excess of iodosylbenzene (1.3 mmol) was added to 1.2 mmol of the chromium(III) complex (Ia–f) dissolved in ~50 mL CH$_3$CN, whereupon the reaction mixture turned from orange to dark green-brown. The slurry was stirred for an additional 30 min and then filtered to remove the unreacted iodosylbenzene. Anhydrous ether (200 mL) was slowly added to the dark filtrate in order to precipitate microcrystals of the oxochromium(V) salts IIa–f in 50–70% yields. The crystals are stable in air, and can be kept in acetonitrile solutions (sealed) at −20 °C for prolonged periods.

The application of this general procedure to the *o*-phenylenediamine analogue Ig afforded a transient dark green-black solution indicative of the presence of an oxochromium(V) complex, but it soom precipitated a brown solid. The sparingly soluble brown solid may be an oxochromium(IV) derivative,[17] which we hope to characterize at a later time. When the soluble oxidant iodobenzenediacetate was used in place of iodosylbenzene, Ig rapidly afforded a similar dark green-black solution. An immediate esr spectrum indeed indicated the formation of a chromium(V) species ($\langle g \rangle$ = 1.977, a_N = 2.05 G), but its rapid decay was accompanied by the formation of a similar brown precipitate. No further attempts were made to isolate the metastable oxochromium(V) salt IIg.

Crystal Structure of [*N*,*N*′-Ethylenebis(salicylidineaminato)]oxochromium(V) Triflate. Among the various oxochromium(V) complexes isolated, we were only able to grow a crystal suitable for X-ray crystallography from the 7,7′-dimethyl analogue IIc. A single crystal of IIc was obtained by the slow evaporation of the solvent in air from a solution consisting of a 1:1 v/v mixture of acetonitrile and chlorobenzene. A small, dark brown-black columnar parallelepiped of approximate dimensions 0.10 × 0.10 × 0.70 mm was mounted on an Enraf-Nonius CAD-4 automatic diffractometer. The Mo Kα radiation was monochromatized by a dense graphite crystal, assumed for all purposes to be 50% imperfect. Final cell constants, as well as other information pertinent to data collection and refinement, are as follows: space group, $P2_1/n$, monoclinic; cell constants, a = 16.233 (2) Å, b = 6.439 (1) Å, c = 19.523 (4) Å, β = 94.44 (1)°, V = 2034.5 Å^3; molecular formula, C$_{19}$H$_{18}$CrF$_3$N$_2$O$_6$S; M_r, 511.41; Z = 4; ρ_{calcd} = 1.67 g cm^{-3}; absorption coefficient, μ = 7.1 cm^{-1}; radiation (Mo Kα), λ = 0.71073 Å; collection range, 4° ≤ 2θ ≤ 42°; scan width, $\Delta\theta = (1.00 + 0.35 \tan \theta)°$; maximum scan time, 300 s; scan speed range, 0.30–3.35° min^{-1}; total number of data collected, 2352; independent data ($I > 3\sigma(I)$), 1741; total number of variables, 362; $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.033$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.031$; $w = \sigma(F)^{-2}$; goodness of fit, 2.9.

The Laue symmetry was determined to be 2/m, and from the systematic absences noted the space group was unambiguously shown to be $P2_1/n$. Intensities were measured by using the θ–2θ scan technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these did not vary significantly. In the reduction of the data, Lorentz and polarization factors were applied, but no correction for absorption was made due to the small absorption coefficient. The structure was solved by use of MULTAN,[18] which revealed the positions of all but two of the non-hydrogen atoms in the asymmetric unit. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were located easily in a difference Fourier synthesis. After all shift/esd ratios were less than 0.1, the full-matrix least squares converged at the agreement factors mentioned above. Anomalous dispersion coefficients for the heavier elements were included. No unusually high correlations were noted between any of the variables in the last cycle of least-squares refinement, and the final difference density map was featureless. All calculations were made by using Molecular Structure Corporation's TEXRAY 230 modification of the SDP-PLUS series of programs. The final positional parameters and their esds are listed in Table I.

Determination of the Formation Constants for the Addition of Donor Ligands to Oxochromium(V) Cations. The addition of various donor ligands D to the oxochromium(V) cation O=CrL$^+$ was monitored by UV–vis spectroscopy. Typically, a 1 × 10^{-3} M solution of the oxochromium(V) complex in acetonitrile contained in a quartz cuvette with a 1-mm path length was treated with successive aliquots of a concentrated standard (1 M) solution of the donor ligand in the same solvent. The weak, lowest energy band of the oxochromium(V) complex exhibited a red shift upon the addition of either pyridine *N*-oxide, triphenylphosphine oxide, or water. The formation of the adduct was evident from the color change (usually from a brown-black solution to an emerald green). The extinction coefficient of the adduct at different wavelengths was obtained

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Table I. Fractional Coordinates and Their Estimated Standard Deviations for Oxochromium(V) Triflate IIc[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Cr	0.74338 (4)	1.0474 (1)	0.32531 (3)	2.88 (1)	C7	0.5955 (2)	1.1784 (6)	0.3985 (2)	3.2 (1)
S	1.24632 (8)	1.1371 (2)	0.46322 (6)	4.19 (3)	C7′	0.9060 (2)	1.1328 (6)	0.4025 (2)	3.1 (1)
F1	1.1796 (2)	1.2752 (6)	0.3464 (2)	8.35 (9)	C8	0.7116 (3)	1.4147 (7)	0.3930 (2)	4.5 (1)
F2	1.3095 (2)	1.2603 (5)	0.3509 (2)	7.92 (9)	C8′	0.7944 (3)	1.3614 (7)	0.4273 (2)	4.0 (1)
F3	1.2504 (2)	1.4959 (4)	0.4039 (2)	8.3 (1)	C9	0.5593 (3)	1.3223 (8)	0.4488 (2)	5.3 (1)
O1	0.7525 (2)	1.1675 (5)	0.2578 (1)	4.21 (7)	C9′	0.9571 (3)	1.2584 (8)	0.4549 (2)	4.8 (1)
O2	0.6601 (2)	0.8622 (4)	0.3120 (1)	3.63 (7)	C10	1.2464 (3)	1.2961 (7)	0.3874 (2)	4.6 (1)
O2′	0.8095 (2)	0.8207 (4)	0.3275 (1)	3.32 (6)	H3	0.555 (2)	0.613 (4)	0.273 (1)	1.2 (6)*
O4	1.3215 (2)	1.1898 (6)	0.5006 (2)	7.0 (1)	H3′	0.895 (2)	0.548 (5)	0.278 (2)	3.1 (8)*
O5	1.1733 (2)	1.2015 (5)	0.4937 (2)	5.81 (9)	H4	0.427 (2)	0.563 (5)	0.300 (2)	3.7 (8)*
O6	1.2429 (2)	0.9318 (5)	0.4362 (2)	6.53 (9)	H4′	1.035 (2)	0.500 (5)	0.284 (2)	5 (1)*
N1	0.6687 (2)	1.2179 (5)	0.3768 (2)	3.21 (8)	H5	0.372 (2)	0.800 (6)	0.370 (2)	6 (1)*
N1′	0.8279 (2)	1.1844 (5)	0.3895 (2)	2.88 (8)	H5′	1.116 (2)	0.758 (7)	0.343 (2)	7 (1)*
C1	0.5492 (2)	0.9972 (6)	0.3734 (2)	3.1 (1)	H6	0.448 (2)	1.056 (5)	0.422 (2)	3.2 (8)*
C1′	0.9409 (2)	0.9595 (7)	0.3684 (2)	2.94 (9)	H6′	1.058 (2)	1.034 (5)	0.395 (2)	3.1 (8)*
C2	0.5816 (2)	0.8544 (6)	0.3292 (2)	3.1 (1)	H8A	0.685 (2)	1.495 (5)	0.424 (2)	4.1 (9)*
C2′	0.8924 (2)	0.8102 (6)	0.3332 (2)	2.86 (9)	H8B	0.718 (2)	1.473 (6)	0.345 (2)	5 (1)*
C3	0.5335 (3)	0.6919 (7)	0.3014 (2)	4.1 (1)	H8A′	0.830 (2)	1.466 (5)	0.430 (2)	3.7 (8)*
C3′	0.9278 (2)	0.6385 (7)	0.3037 (2)	3.6 (1)	H8B′	0.794 (2)	1.318 (6)	0.477 (2)	5 (1)*
C4	0.4539 (3)	0.6708 (7)	0.3178 (2)	4.8 (1)	H9A	0.533 (2)	1.415 (7)	0.431 (2)	7 (1)*
C4′	1.0124 (3)	0.6145 (7)	0.3084 (2)	4.4 (1)	H9B	0.599 (2)	1.358 (5)	0.493 (2)	4.4 (9)*
C5	0.4207 (3)	0.8091 (8)	0.3613 (2)	5.3 (1)	H9C	0.523 (2)	1.256 (6)	0.474 (2)	6 (1)*
C5′	1.0613 (3)	0.7607 (8)	0.3416 (2)	4.6 (1)	H9A′	0.987 (2)	1.368 (5)	0.435 (2)	3.0 (8)*
C6	0.4668 (3)	0.9668 (7)	0.3887 (2)	4.2 (1)	H9B′	1.008 (2)	1.201 (6)	0.468 (2)	6 (1)*
C6′	1.0279 (3)	0.9284 (7)	0.3716 (2)	4.0 (1)	H9C′	0.930 (2)	1.288 (6)	0.493 (2)	5 (1)*

[a] Starred parameters were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

by measuring the absorbances of solutions containing a large excess of donor (i.e., under conditions in which incremental additions did not affect the absorbance). The individual concentrations C_u and C_c of the uncoordinated species $O{=}CrL^+$ and the coordinated species $O{=}CrL(D)^+$, respectively, were calculated by solving the simultaneous equations[19] $\epsilon_u C_u + \epsilon_c C_c = A$ and $\epsilon_u' C_u' + \epsilon_c' C_c' = A'$, where ϵ_u, ϵ_u' and ϵ_c, ϵ_c' are the extinction coefficients of the uncoordinated and coordinated species, respectively, and A and A' are the absorbances of the pair of overlapping bands at the monitoring wavelengths λ and λ'.

Crystal Structure of the Oxochromium(V) Adduct of Pyridine *N*-Oxide. Among the various oxochromium(V) complexes IIa–f, we were only able to isolate the adduct of the dichlorotetramethyl analogue IIf with pyridine *N*-oxide. A single crystal suitable for X-ray crystallography was grown by carefully adding 10 mL of hexane as a separate layer onto a CH_2Cl_2 solution of 0.014 M IIf and 0.2 M pyridine *N*-oxide. Partial diffusion occurred over 3 days at −20 °C to produce a small crop of large dark-green needles. A square columnar rod of approximate dimensions 0.60 × 0.25 × 0.25 mm was mounted on a glass fiber for crystallographic analysis as described above. The final cell constants, as well as other information pertinent to data collection and refinement are as follows: space group, $P4_32_12$, tetragonal; cell constants, a = 11.938 (1) Å, c = 43.366 (9) Å, V = 6174 Å^3; molecular formula, $CrCl_2SF_3O_7N_3C_{26}H_{25}$; fw, 703.46; Z = 8; ρ = 1.52 g cm^{-3}; absorption coefficient, μ = 6.85 cm^{-1}; radiation (Mo Kα), λ = 0.71073 Å; collection range, $4° < 2\theta < 45°$; scan width, $\Delta\theta = (0.70 + 0.35 \tan\theta)°$; maximum scan time, 90 s; scan speed range, 0.7–5.0° min^{-1}; total number of data collected, 2464; number of independent data ($I > 3\sigma(I)$), 1240; number of total variables, 388; $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.044$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.037$; $w = \sigma(F)^{-2}$.

The Laue symmetry was determined to be $4/mmm$, and from the systematic absences noted the space group was shown to be either $P4_12_12$ or the enantiomorphous $P4_32_12$. Intensities were measured by using the ω scan technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these did not vary significantly. In the reduction of the data, Lorentz and polarization factors were applied. However, no correction for absorption was made due to the small absorption coefficient. One unique sixteenth of the reciprocal sphere was collected, consisting of the nonnegative *hkl*'s having $k > h$. The structure was solved by MULTAN,[18] which revealed the positions of one-half of the non-hydrogen atoms in the asymmetric unit. The remaining atoms were located in subsequent difference Fourier synthesis. All preliminary refinement was done assuming $P4_12_12$ to be the correct space group. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideally calculated positions. Owing to an unfortunate quirk in the SDP programs, the sulfur atom had to be refined as Cl with a 94% population factor. Since there were not many observed data, the hydrogens were held fixed in all of the cycles of full-matrix least squares. After all shift/esd ratios were less than 0.1, convergence was reached at R = 4.7% and R_w = 4.0%. At this point, the atomic coordinates were inverted and the refinement was repeated in space group $P4_32_12$, with the scale factor fixed. This resulted in agreement factors of R = 4.4% and R_w = 3.7%, which was a significant improvement. Verification of $P4_32_12$ was provided by performing the Bijovet test[20] on six strong reflections affected by anomalous dispersion, each of which indicated that $P4_12_12$ was indeed the incorrect choice. The correct absolute configuration of this chiral molecule is thus determined to be left-handed with respect to the N–C–C–N moiety (negative torsion angle), as shown in Figure 6. No unusually high correlations were noted among any of the variables in the last cycle of least-squares refinement, and the final difference density map showed no peaks greater than 0.23 e A^{-3}. The final positional parameters and their esds are listed in Table II.

Oxygen-18 Labeling Studies of [*N*,*N*′-Ethylenebis(salicylideneaminato)]chromium(III) and -Oxochromium(V) Complexes. Synthesis of [(8,8,8′,8′-Me$_4$salen)Cr(^{18}OH$_2$)$_2$]OTf (Ie). A solution of [(8,8,8′,8′salen)Cr(OH$_2$)$_2$]OTf (Ie) (0.091 mmol) in 3 mL of acetonitrile was treated with 1.0 × 10^{-1} mL (0.55 mmol) of ^{18}O-enriched (90%) water (Aldrich). The solution was stirred for 4 h, after which the solvent was removed in vacuo to afford a dry yellow sample. Owing to the broadness of the IR band, the aquo ligands of Ie were merely estimated to be ~75% enriched in ^{18}OH$_2$.

Synthesis of ^{18}O═Cr(Me$_4$salen)OTf (IIe). A solution of oxochromium(V) IIe (0.036 mmol) in 3 mL of acetonitrile was treated with 50 μL of ^{18}O-enriched (90%) water. An aliquot was removed after 2 h and the solvent removed in vacuo and replaced with methylene chloride. Infrared analysis of the ^{18}O═Cr and ^{16}O═Cr stretching bands at 965 and 1006 cm^{-1}, respectively, indicated ~20% exchange. However, an analysis after 8 h indicated ~85% exchange. After 12 h, the mixture was worked up to afford crystalline IIe with ~85% enrichment of the ^{18}O═Cr functionality. A control experiment carried out with the same amount of added ^{16}OH$_2$ under identical conditions indicated that IIe could be recovered unchanged without significant decomposition.

Preparation of [(5,5′-Cl$_2$-8,8,8′,8′-Me$_4$salen)Cr═^{18}O]OTf (IIf). The oxochromium(V) IIf (0.97 mmol, 600 mg) in 150 mL of CH_3CN was treated with 2.0 g of ^{18}O-enriched (90%) water. The resulting light green solution was stirred under argon for 24 h at 25 °C. Addition of Linde 4A molecular sieves caused the green color of the solution to change to black, indicative of the removal of water. The solution was filtered and

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(19) See, e.g.: Foster, R. "Organic Charge Transfer Complexes"; Academic Press, New York, 1969.

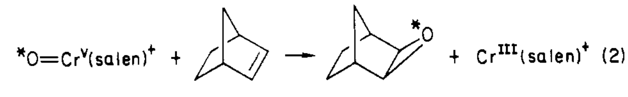
(20) Bijvoet, J. M.; Peedeman, A. F.; Van Bommel, A. J. *Nature (London)* **1951**, *168*, 271.

Table II. Fractional Coordinates and Their Estimated Standard Deviations for the Adduct of Oxochromium(V) Triflate IIf with Pyridine *N*-Oxide[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Cr	0.2444 (2)	0.8691 (1)	0.84423 (3)	3.42 (4)	C9′	0.5409 (9)	0.726 (1)	0.8026 (3)	6.4 (3)
Cl1	−0.1934 (3)	0.5082 (3)	0.89884 (9)	9.0 (1)	C10	0.3866 (9)	0.5404 (8)	0.8362 (2)	4.4 (3)
Cl1′	0.4935 (4)	1.3238 (3)	0.76013 (9)	11.4 (1)	C10′	0.499 (1)	0.7406 (9)	0.8589 (2)	6.0 (3)
S	0.4710 (3)	0.9235 (3)	0.96433 (7)	7.2 (1)	C11	0.033 (1)	0.7832 (8)	0.7798 (2)	5.7 (3)
F1	0.6582 (8)	0.8232 (9)	0.9735 (2)	18.1 (4)	C12	−0.083 (1)	0.785 (1)	0.7725 (2)	7.2 (4)
F2	0.6259 (8)	0.8612 (9)	0.9282 (2)	16.6 (4)	C13	−0.1431 (9)	0.882 (1)	0.7757 (2)	6.7 (4)
F3	0.527 (1)	0.7322 (7)	0.9493 (3)	19.2 (4)	C14	−0.0843 (9)	0.976 (1)	0.7855 (3)	7.5 (4)
O1	0.2898 (5)	0.8641 (5)	0.8778 (1)	4.4 (2)	C15	0.029 (1)	0.9661 (9)	0.7920 (2)	5.8 (3)
O2	0.0924 (5)	0.8688 (5)	0.8519 (1)	4.0 (2)	C16	0.577 (2)	0.840 (1)	0.9554 (3)	17.6 (7)
O2′	0.2392 (6)	1.0221 (5)	0.8389 (1)	4.2 (2)	H3	−0.0937	0.8840	0.877	5*
O3	0.1947 (5)	0.8669 (5)	0.7960 (1)	4.0 (2)	H3′	0.1934	1.2213	0.8235	5*
O4	0.3951 (7)	0.9209 (7)	0.9391 (2)	8.7 (3)	H4	−0.2105	0.7417	0.8963	5*
O5	0.4352 (9)	0.8859 (9)	0.9930 (2)	12.0 (4)	H4′	0.2942	1.3380	0.7916	5*
O6	0.541 (1)	1.0318 (8)	0.9659 (2)	16.2 (4)	H6	0.0180	0.5118	0.8699	5*
N1	0.2514 (6)	0.7017 (6)	0.8383 (1)	2.9 (2)	H6′	0.5231	1.0954	0.7767	5*
N1′	0.3886 (7)	0.8543 (6)	0.8230 (2)	3.6 (2)	H7	0.1807	0.5595	0.8438	5*
N2	0.0848 (7)	0.8705 (7)	0.7896 (2)	4.6 (2)	H7′	0.5022	0.9186	0.7964	5*
C1	0.0683 (8)	0.6717 (8)	0.8605 (2)	3.1 (2)	H9A	0.2586	0.5786	0.7868	5*
C1′	0.3925 (9)	1.0473 (8)	0.8055 (2)	4.1 (3)	H9B	0.2951	0.7148	0.7792	5*
C2	0.0333 (8)	0.7859 (8)	0.8631 (2)	3.6 (3)	H9C	0.3938	0.6108	0.7768	5*
C2′	0.2957 (8)	1.0832 (8)	0.8199 (2)	3.2 (3)	H9A′	0.6013	0.7880	0.8060	5*
C3	−0.0702 (8)	0.8080 (9)	0.8762 (2)	4.6 (3)	H9B′	0.5765	0.6465	0.8062	5*
C3′	.2606 (9)	1.1943 (8)	0.8142 (2)	4.3 (3)	H9C′	0.5090	0.7307	0.7801	5*
C4	−0.1400 (9)	0.7236 (9)	0.8872 (2)	5.7 (3)	H10A	0.3203	0.4834	0.8335	5*
C4′	0.322 (1)	1.264 (1)	0.7957 (2)	5.9 (3)	H10B	0.4573	0.5109	0.8244	5*
C5	−0.1055 (9)	0.6135 (9)	0.8842 (2)	6.0 (3)	H10C	0.4051	0.5498	0.8596	5*
C5′	0.421 (1)	1.231 (1)	0.7830 (2)	6.2 (3)	H10A′	0.5621	0.8019	0.8599	5*
C6	−0.0039 (9)	0.5884 (8)	0.8716 (2)	4.6 (3)	H10B′	0.4373	0.7580	0.8753	5*
C6′	0.457 (1)	1.1210 (9)	0.7871 (2)	6.2 (3)	H10C′	0.5335	0.6615	0.8628	5*
C7	0.1706 (8)	0.6381 (9)	0.8467 (2)	3.6 (3)	H11	0.0733	0.7150	0.7775	5*
C7′	0.4353 (9)	0.9356 (9)	0.8072 (2)	4.6 (3)	H12	−0.1198	0.7186	0.7657	5*
C8	0.3512 (8)	0.6557 (8)	0.8227 (2)	3.5 (3)	H13	−0.2207	0.8852	0.7715	5*
C8′	0.4446 (8)	0.7433 (9)	0.8257 (2)	3.7 (3)	H14	−0.1212	1.0466	0.7872	5*
C9	0.3219 (9)	0.6384 (9)	0.7887 (2)	4.9 (3)	H15	0.0697	1.0306	0.7983	5*

[a] See footnote *a* in Table I.

concentrated in vacuo to ~40 mL. The addition of freshly distilled anhydrous ether (100 mL) afforded 0.37 g (0.59 mmol, 60%) of a black solid with the characteristic $^{18}O{=}Cr$ and $^{16}O{=}Cr$ IR stretching bands at 965 and 1004 cm^{-1}, respectively, with an intensity ratio of 8.0:2.0 in methylene chloride. The reaction of this labeled oxochromium(V) with norbornene afforded essentially quantitative yields of norbornene oxide, which showed 80% ^{18}O incorporation by GC-MS analysis, i.e.



(2)

The same results were obtained when 5 equiv of pyridine *N*-oxide was used as the cocatalyst.[5]

Cyclic Voltammetry of Oxochromium(V) Cations. Cyclic voltammetry was performed in a cell designed according to Van Duyne and Reilly.[21] The distance between the Pt electrode and the tip of the salt bridge was less than 2 mm to minimize the ohmic drop in the nonaqueous solution. The SCE reference electrode was maintained at room temperature and connected to the potentiostat by means of a high-impedance voltage follower amplifier (PAR Model 178) with a minimum length of connector for low noise pickup. All solutions contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. The pollution of the electrode during the reduction of oxochromium(V) could be reduced, but not eliminated, if the CV studies were carried out with the cell immersed in an ice bath (with the reference cell mounted externally).

Results and Discussion

I. Formation of Oxochromium(V) Cations. The rapid, efficient synthesis of a variety of (salen)Cr^{III} cationic complexes Ia–g (as the salts of the noncoordinating triflate anion[22,23]) is based on the treatment of the substitution-labile chromium(II) triflate with the free ligand in a nonaqueous medium, followed by direct aerial oxidation in situ and isolation as the dihydrate,[24] i.e.

$$Cr(OTf)_2 + H_2salen \xrightarrow{\text{fast}} [(salen)Cr^{II}] \xrightarrow{O_2} \xrightarrow{H_2O} \underset{\text{Ia–g}}{(salen)Cr(OH_2)_2{}^+OTf^-} \quad (3)$$

Table III. Oxygen-18 Tracer Studies of Oxochromium(V) Formation from (salen)Cr^{III}(OH$_2$)$_2{}^+$ and Iodosylbenzene[a]

% ^{18}O enrichment of reactants		% oxochromium(V)	
(salen)Cr(OH$_2$)$_2{}^+$	PhIO	^{18}O	^{16}O
0	85	15	85
75	85	60	40
~75	0	25	75

[a] In acetonitrile (1 mL) containing 0.036 mmol of IIe and 0.041 mmol of PhIO.

Its subsequent conversion to the corresponding oxochromium(V) cations IIa–f can be effected with either iodosylbenzene or *m*-chloroperbenzoic acid in acetonitrile,[3] i.e.

$$(salen)Cr(OH_2)_2{}^+ + PhIO \rightarrow O{=}Cr(salen)^+ + PhI + 2H_2O \quad (4)$$

For synthetic purposes, iodosylbenzene is the preferred oxygen donor owing to its insolubility (which allows the unreacted material to be easily removed prior to workup) and the ready separation of the innocuous iodobenzene from the oxochromium(V) salts IIa–f. The triflate salt I is particularly useful for oxochromium(V) synthesis since it is readily soluble in acetonitrile. However the

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(21) Van Duyne, R. P.; Reilly, C. N. *Anal. Chem.* **1972**, *44*, 142.

(22) See: Scott, A.; Taube, H. *Inorg. Chem.* **1971**, *10*, 62.

(23) In the absence of added water, the [*N*,*N*′-ethylenebis(salicylideneaminato)]chromium(III) triflate is obtained as an intractable, amorphous-looking brown solid.

(24) The modification derives from a procedure reported by Dey and coworkers.[25]

(25) Dey, K., De, R. L.; Ray, K. C. *Indian J. Chem.* **1972**, *10*, 864.

Table IV. Spectral Parameters and the Magnetic Susceptibility of Oxochromium(V) Cations

	IR[a]	vis[b]		ESR[b]			
O=Cr^V(salen)$^+$	$\nu_{O=Cr}$, cm^{-1}	λ, nm	ε, M^{-1} cm^{-1}	$\langle g \rangle$	a_N, G	a_{Cr}, G	μ_{eff},[b] m_B
IIa	998	566	1200	1.978	2.17	19.42	1.75
IIb	1007	558	2300	1.978	2.15	19.50	1.82
IIc	1003	548	1765	1.978	2.15	19.35	1.85
IId	985	550	1650	1.978	2.05	19.25	1.86
IIe	1007 1006[c]	550	1225	1.977	2.18	19.87	1.76
IIf	1006	540	(2050)	1.979	2.15	19.90	

[a] Nujol mull. [b] CH_3CH solution. [c] CH_2Cl_2 solution.

presence of a pair of aquo ligands (eq 3) does raise the mechanistic question of whether the oxo ligand is derived from iodosylbenzene or from the bound water. To attempt a resolution of this question, we used oxygen-18 as an isotopic tracer, e.g.

$$(salen)Cr(OH_2)_2^+ + {}^*OIPh \rightarrow {}^*O{=}Cr(salen)^+ + PhI \qquad (5)$$

The first entry in Table III indicates that a direct oxygen atom transfer from iodosylbenzene to chromium(III) as in eq 5 is apparently inefficient. However, the third entry in Table III does not support the bound water in I as the sole source of the oxo ligand as dictated by

$$(salen)Cr({}^*OH_2)_2^+ + PhIO \rightarrow {}^*O{=}Cr(salen)^+, \text{etc.} \qquad (6)$$

This apparent inconsistency is resolved by the observation that the oxo ligand in II is exchanged readily with water,[26] i.e.

$$O{=}Cr(salen)^+ + {}^*OH_2 \rightarrow {}^*O{=}Cr(salen)^+ + OH_2 \qquad (7)$$

Thus, independent experiments show that isotopically labeled oxochromium(V) IIf undergoes complete exchange of its oxygen-18 with ordinary water (10 equiv) in acetonitrile solutions within 8 h. Although the ready exchange in eq 7 effectively vitiates the isotopic tracer studies, it does provide an efficient and simple procedure for the synthesis of ^{18}O-labeled oxochromium(V) complexes as a source for ^{18}O incorporation into various substrates (cf. eq 2). Moreover the efficacy with which (salen)Cr^{III} does catalyze the epoxidation of olefins with iodosylbenzene[5] strongly supports the pathway involving direct oxygen atom transfer.

II. Spectroscopic Properties of Oxochromium(V) Cations. The conversion of (salen)Cr^{III} to O=Cr^V(salen) is accompanied by diagnostic changes in the infrared spectrum in the region between 900 and 1020 cm^{-1}. Thus [*N*,*N*′-ethylenebis(salicylidineaminato)]chromium(III) triflates show no absorption in this range whereas a sharp stretching band for the terminal O=Cr bond appears typically at 1000 cm^{-1}, as listed in Table IV, for the various oxochromium(V) cations IIa–f.[27] Isotopic substitution with oxygen-18 in IIe leads to a shift in the stretching vibration from 1007 to 966 cm^{-1}, which accords with the theoretical prediction of $\nu_{18} \simeq 0.95\nu_{16}$.[28] Oxochromium(V) complexes isolated in this manner show a pair of sharp bands at 1033 and 1273 cm^{-1} for the ν_1 (A_1) and ν_4 (E) stretching vibrations of the uncoordinated triflate ion,[29] but no absorptions in the region 3200–3500 cm^{-1} for coordinated water are apparent.

The electronic spectra of oxochromium(V) cations IIa–f in acetonitrile solutions are characterized by a very broad, featureless absorption extending from 500 to beyond 800 nm with an unresolved maximum (shoulder) at ~500 nm ($\epsilon = 2 \times 10^3$ M^{-1} cm^{-1}).

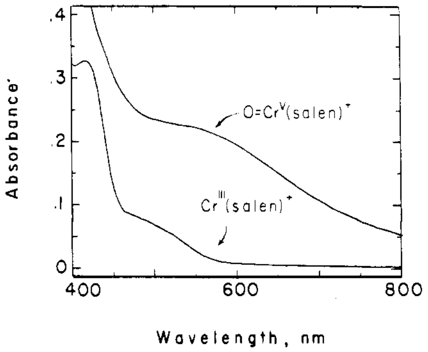

Figure 1. Electronic absorption spectrum of 1.2 × 10^{-3} M Cr^{III}(salen)$^+$ in acetonitrile (lower spectrum) and 1.2 × 10^{-3} M O=Cr^V(salen)$^+$ (upper spectrum).

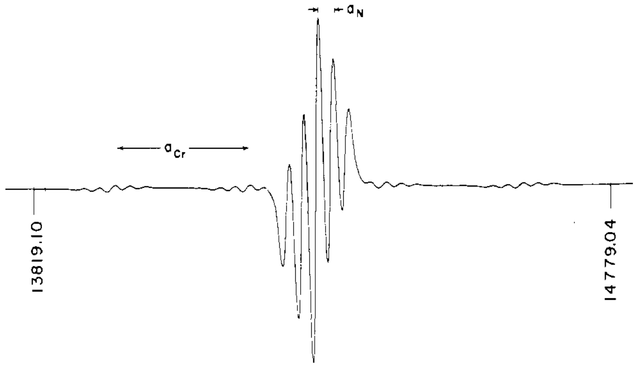

Figure 2. Isotropic ESR spectrum of O=Cr^V(Me$_4$salen)$^+$ (IIe) in acetonitrile solution at 25 °C, showing the well-resolved ^{53}Cr ($I = {}^3/_2$, 9.55% natural abundance) and ^{14}N hyperfine splittings. ^{1}H NMR field markers are in kHz.

The absorption spectrum is unchanged in methylene chloride solution. Related solvent-independent absorptions of simple chromyl complexes have been assigned to d–d transitions.[30] However there is a recent suggestion that the absorption bands in the region about 500–600nm in oxochromium(V) corroles are due to Cr (d)–ligand π^* charge-transfer transitions.[31] The direct comparison with the absorption spectrum of the (salen)Cr^{III} precursor shown in Figure 1 underscores the striking and diagnostic color change attendant upon the oxygen atom transfer to afford the oxochromium(V) species.

The formation of oxochromium(V) species can also be readily diagnosed in solution by the appearance of an isotropic ESR spectrum at room temperature. Figure 2 shows a typical, well-resolved ESR spectrum of the oxochromium(V) cation in acetonitrile showing a quintet splitting due to two equivalent nitrogens (a_N = 2.15 G) centered at $\langle g \rangle$ = 1.978, accompanied by a four-component hyperfine structure arising from the ^{53}Cr isotope ($I = {}^3/_2$) in 9.55% natural abundance. The ESR parameters listed in Table IV are characteristic of other d^1 chromium(V) complexes.[32] Moreover the experimental magnetic susceptibilities determined by the Evans method and listed in Table IV also accord with the calculated spin-only value of 1.73 μ_B for the chromium(V) complex.[33-35]

III. Coordination of Donor Ligands to Oxochromium(V) Cations. The rapid interaction of neutral donor ligands D, such

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(26) A similar exchange of oxochromium(V) with water was previously reported for the porphyrin complex by Groves et al.[3]

(27) (a) In the porphyrin complex, the O=Cr stretching vibration occurs at 1026 cm^{-1}, which is shifted to 982 cm^{-1} upon conversion to the ^{18}O-labeled complex.[3] (b) See also: Matsuda, Y.; Yamada, S.; Murakami, Y. *Inorg. Chim. Acta* **1980**, *44*, 1309. (c) For IR stretching frequencies of O=Cr in other oxochromium(V) complexes, see ref 2.

(28) Herzberg, G. "Molecular Spectra and Molecular Structure, Part II. Infrared and Raman Spectra of Polyatomic Moleculars"; Van Nostrand: New York, 1945; p 229.

(29) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969.

(30) Bramman, P. F.; Lund, T.; Raynor, J. B.; Willis, C. J. *J. Chem. Soc., Dalton Trans.* **1975**, 45.

(31) Murakami, Y.; Matsuda, Y.; Yamada, S. *J. Chem. Soc., Dalton Trans.* **1981**, 855.

(32) For leading references, see: Miyaura, N.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 2368.

(33) (a) Green, P. J.; Johnson, B. M.; Loehr, T. M.; Gard, G. L. *Inorg. Chem.* **1982**, *21*, 3562. (b) Ziebarth, O. V.; Selbin, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 849.

(34) Seddon, K. R.; Thomas, V. H. *Inorg. Chim. Acta* **1976**, *20*, L37; *J. Chem. Soc., Dalton Trans.* **1977**, 2195.

(35) Krumpolc, M.; DeBoer, B. G.; Roček, J. *J. Am. Chem. Soc.* **1978**, *100*, 145.

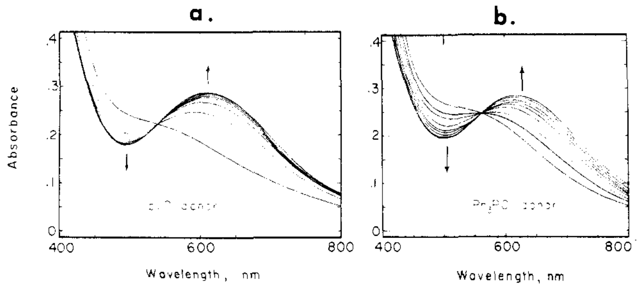

Figure 3. Spectral changes accompanying adduct formation of oxochromium(V) with donor ligands in acetonitrile: (a) 1.2 × 10^{-3} M O=Cr(Ph_2salen)$^+$ with (bottom to top) 0, 1, 2, 3, 5, 10, 30, and 40 (60, 70, 80) equiv of pyridine *N*-oxide; (b) 1.2 × 10^{-3} M O=Cr(salen)$^+$ with (bottom to top) 0, 1, 4, 6, 8, 10, 14, and 20 equiv of triphenylphosphine oxide.

Table V. Spectral Parameters of the Adducts of Donor Ligands to Oxochromium(V) Cations^a

O=Cr(salen)$^+$	donor ligand	λ, nm (ε, M^{-1} cm^{-1})	$\nu_{O=Cr}$, cm^{-1}	ESR		
				g	a_{Cr}, G	a_N, G
IIa	pyO	610 (2490)	939^b	1.975	19.42	1.97
	Ph_3PO	616 (2364)				
	Me_2SO			1.975	19.37	2.01
IIe	pyO	628 (1722)	942	1.975	19.79	1.94
	Et_3PO		942	1.974	19.75	1.85
IIf	pyO	650 (2550)	942			
	pyO	...	901^c			

^{a} In CH_3CN solution. ^{b} In CH_3CN, $\nu_{O=Cr}$ 1000 cm^{-1} for IIa. ^{c} For the ^{18}O oxochromium (V) species.

as pyridine *N*-oxide, triphenylphosphine oxide and water, to the oxochromium(V) cation is visually apparent in acetonitrile solution by the pronounced and immediate color change from almost black to emerald green. The change in the electronic absorption corresponds to a red shift in λ_{max} ~ 550 nm for the oxochromium(V) cation Ia to 600 nm. Upon the incremental addition of either pyridine *N*-oxide or triphenylphosphine oxide as the donor ligand, the change in the absorption spectrum results in a single, well-defined isobestic point, as shown in parts a and b of Figure 3, respectively. Coupled with the quantitative analysis of the absorbance change (see Experimental Section), we conclude the reversible formation of a 1:1 adduct, i.e.

$$O{=}Cr(salen)^+ + D \overset{K}{\rightleftharpoons} O{=}Cr(salen)D^+ \tag{8}$$

Adduct formation is accompanied by corresponding changes in the infrared and ESR spectra. Thus the O=Cr stretching vibration in IIe is decreased to 942 cm^{-1}, which corresponds to a weakening of the oxo-chromium bond by almost 0.2 kcal mol^{-1} upon coordination by pyridine *N*-oxide. It is noteworthy that triethylphosphine oxide has the same effect, as listed in Table V. Adduct formation also leads to a slight shift in the esr spectrum from $\langle g \rangle$ = 1.978–1.975. Although there is no significant change in the ^{53}Cr hyperfine splitting (see Table V), there is a decrease in the nitrogen hyperfine splitting suggestive of a diminished spin density on the salen ligand. (The latter could be a signal for an increased spin density in the oxo ligand.[36])

The formation constants *K* for the oxochromium(V) adducts in Table VI were determined in acetonitrile solutions by the spectrophotometric analyses of the absorption spectra (see Experimental Section). The value of *K* = 1250 M^{-1} for the pyridine *N*-oxide adduct of O=Cr(salen)$^+$ was verified by an independent analysis of the series of overlapping ESR spectra obtained from the incremental addition of pyridine *N*-oxide (compare ESR parameters in Tables IV and V.) We judge from the magnitude of the formation constants *K* in Table VI that the oxochromium(V) cation forms a somewhat stable adduct with pyridine *N*-oxide.

Table VI. Formation Constants of Cationic Adducts from Oxochromium(V) Cations and Neutral Donor Ligands^a

O=Cr(salen)$^+$	*K*, M^{-1}		
	pyO	Ph_3PO	H_2O
IIa	1250 ± 210	440 ± 112	5 ± 2
IIb	1200 ± 200	400 ± 100	5 ± 2
IIc	1260 ± 250	220 ± 75	2.2 ± 0.4
IId	900 ± 150	105 ± 46	1.5 ± 0.5
IIe	75 ± 18	13 ± 13	0.1 ± 0.05

^{a} In acetonitrile at 25 °C.

Table VII. Spectral Parameters of the Adducts of Oxochromium(V) Cations with Anionic Donor Ligands^a

O=Cr(salen)$^+$	chloride λ (ε)^b	trifluoroacetate λ (ε)^b	fluoride		
			λ_1^{c}	λ_2^{d}	a_F^{e}
IIa	644 (2300)	622 (2300)	614	606	3.60
IIb	678 (1700)	642 (2300)	634	608	3.60
IIc	632 (1600)	592 (1600)	600	590	3.80^f
IId	646 (2300)	620 (2500)	606	602	3.70^g
IIe	*i*	*i*	614	614	3.50^h

^{a} As either the tetraethylammonium or sodium salt in CH_3CN solution at 25 °C. ^{b} λ in nm and ε in M^{-1} cm^{-1}. ^{c} Absorption maximum (nm) for the reaction with 1 equiv of fluoride. ^{d} Absorption maximum (nm) for the reaction with 2 equiv of fluoride. ^{e} Fluorine splitting (G) in the ESR spectrum for the final adduct. All have $\langle g \rangle$ = 1.974 and a_N = 1.75 G, unless stated otherwise. ^{f} a_N = 1.90 G. ^{g} a_N = 1.86 G. ^{h} a_N = 1.69 G. ^{i} Adduct decomposes too fast to measure.

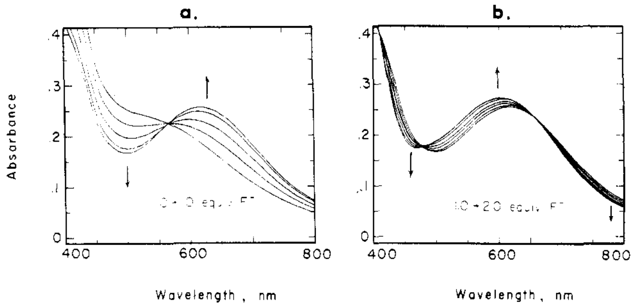

Figure 4. Spectral changes accompanying incremental additions of fluoride to 1.2 × 10^{-3} M O=Cr(salen)$^+$ (IIa) in acetonitrile: (a) 0, 0.25, 0.50, 0.75, and 1.0 equiv of fluoride; (b) 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 equiv of fluoride.

The trend in *K* (see column 2 especially) indicates a significant steric inhibition by methyl substituents on the ethano bridge of the salen ligand. However, the electronic effects of substituents on the adduct formation do not appear to be pronounced. Triphenylphosphine oxide adducts are consistently less stable than their pyridine *N*-oxide counterparts. Significantly, water is the least effective among the three donor ligands.[37]

Anions such as halide and carboxylate also form adducts with oxochromium(V) cations that show varying degrees of persistence. For example, the addition of 1 equiv of chloride as the tetraethylammonium salt to the oxochromium(V) cation IIa in acetonitrile leads to (1) an immediate, large red shift in the visible absorption band (Table VII), (2) a shift in $\nu_{O=Cr}$ from 1000 to 939 cm^{-1} and (3) a concomitant appearance of a new ESR spectrum ($\langle g \rangle$ = 1.972, a_N = 1.85 G) diagnostic of an oxochromium(V) adduct. The shape of the spectral titration curve indicates the formation of a strongly bound 1:1 adduct, e.g.

$$O{=}Cr(salen)^+ + Cl^- \rightarrow O{=}Cr(salen)Cl \tag{9}$$

The addition of excess chloride causes no further change in the spectra. However both the ESR signal and the low-energy band in the electronic spectrum decay rather rapidly to an unidentified

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(36) In this regard, it would be interesting to examine the ESR spectrum of the ^{17}O-labeled oxochromium(V) species.

(37) For the measurement of the formation constants for related adducts with the isoelectronic vanadyl system in $VO(acac)_2$ complexes, see: Carlin, R. L.; Walker, F. A. *J. Am. Chem. Soc.* **1965**, *87*, 2128. See also ref 41.

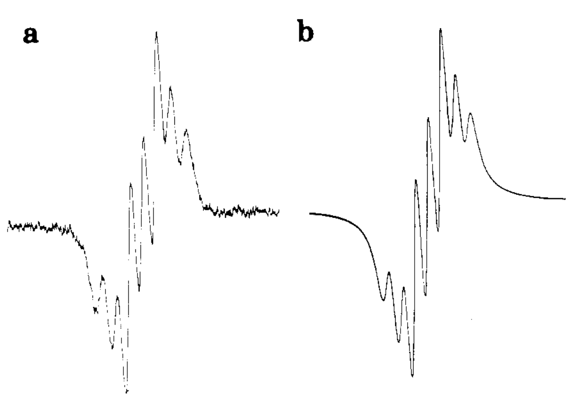

Figure 5. ESR spectrum of the fluoride adduct to oxochromium(V) IIa with resolved hyperfine splittings from a single fluorine: (a) experimental spectrum at $\langle g \rangle = 1.974$ of the adduct from the isotopic ^{53}Cr species in acetonitrile at 25 °C; (b) computer-simulated ESR spectrum with hyperfine splittings $a_N = 1.79$ G and $a_F = 3.63$ G (peak to peak line widths of 1.3 G) superimposed on a broad envelope (with 5.8 G line width) in a ratio of 9:2.

chromium(III) product. The addition of sodium trifluoroacetate to IIa forms a similar unstable adduct as indicated by significant shifts in both the visible and ESR spectra (Table VII).

The behavior of fluoride as a donor ligand is unique and somewhat puzzling. Thus the addition of 1 equiv of fluoride (as $Et_4NF{\cdot}2H_2O$[38]) to a dark (black) acetonitrile solution of the oxochromium(V) cation IIa causes an immediate change to green.[39] The changes in the visible spectrum of IIa accompanying the incremental addition of up to 1 equiv of fluoride are detailed in Figure 4a. The infrared band $\nu_{O=Cr}$ also shifts from 1000 to 942 cm^{-1} upon the addition of 1 equiv of fluoride, but no discrete ESR signal could be observed (even down to −40 °C). However, the measurement of the magnetic susceptibility ($\mu_{eff} = 1.78\ \mu_B$) of this solution by the Evans method indicates that a chromium(V) species is still present. (A fast-exchange process could account for this diverse magnetic behavior.) The addition of a second 1 equiv of fluoride brings about another change in color from the green in Figure 4a to blue. The new visible spectrum now shows a small blue shift, as indicated by the successive spectral changes attendant upon the incremental addition of up to 2 equiv of fluoride in Figure 4b. There is no change upon the addition of excess (i.e., >2 equiv) fluoride. Upon the addition of the second equivalent of fluoride, a new complex ESR spectrum, shown in Figure 5a, is obtained. The successful computer simulation of the spectrum in Figure 5b indicates the presence of an additional splitting of $a_F = 3.60$ G arising from a single fluorine atom. These adducts decompose quite rapidly at room temperature, as judged by the decay of the ESR signal as well as by the diminution of the low-energy band of the visible absorption spectrum. Similar changes are also noted with the other oxochromium(V) cations listed in Table VII. The observation of the well-defined isosbestic points in the visible spectra shown in Figure 4 indicate the formation of at least two adducts during the incremental addition of up to 2 equiv of fluoride to the oxochromium(V) cations. The hyperfine splittings arising from a single fluorine in the esr spectra of the second species is suggestive of an addend similar to that presented in eq 9. Such a structural assignment however leaves unanswered the question of the identity of the first adduct.[40] We hope that further studies will resolve this conundrum.

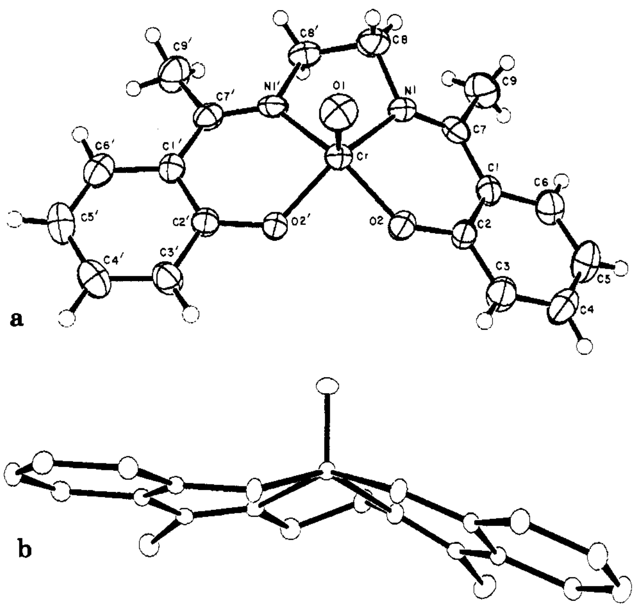

Figure 6. ORTEP diagram of the oxochromium(V) cation from IIc: (a) top perspective; (b) side view with the hydrogen atoms removed for clarity.

Finally, the metastable character of the oxochromium(V) adducts derived from anionic ligands does underscore the necessity of employing *cationic* (salen) Cr^{III} complexes in synthetic procedures. Thus any attempt to effect oxygen atom transfer to a neutral (salen)Cr^{III} complex such as $ClCr^{III}$(salen) would not be able to overcome competition from the facile decomposition of the oxo–chromium(V) adduct.

IV. Molecular Structures of the Oxochromium(V) Cation and Its Adduct with a Donor Ligand: A Comparison. The 7,7′-Me_2salen complex of the oxochromium(V) triflate (IIc) afforded a single crystal that did not suffer from the disorder which we previously experienced with the parent complex O═Cr(salen)PF_6.[4] Accordingly the ORTEP diagram of IIc in Figure 6 is presented in two orientations, with the upper view clearly delineating the location of the principal atoms. The lower perspective emphasizes four important features of the oxochromium(V) structure—(a) the discrete oxo–chromium functionality, (b) the square-pyramidal configuration of the chromium center, (c) the quasi-planar nature of the salen ligand, and (d) the displacement of the chromium atom above the square plane defined by the pair of oxygen atoms (O2 and O2′) and nitrogen atoms (N1 and N1′) in the salen ligand. Indeed these gross features are the same as those presented earlier.[4] In particular, the Cr displacement of 0.533 (1) Å and O–Cr bond distance of 1.545 Å are actually close to the averages found previously for the two different O═Cr sites in the disordered structure.[41] Both structural features are also present in the oxochromium(V) complexes $K[OCr^V(O_2CC(O)(Me)Et)_2]H_2O$[35] and $Ph_4As[Cr^VCl_4O]$.[42] The structure of the salen skeleton in IIc is similar to that found in the chromium(III) complex $[Cr^{III}(salen)(H_2O_2)]Cl$,[7] in which it exists in a flattened half-chair or stepped conformation.[43] (Note; the chromium atom is located in the plane of the salen ligand in this complex.) Although the Cr–N1 and Cr–N1′ distances in IIc of 1.969 and 1.991 Å are similar to those (2.005 and 1.997 Å) found in $[Cr^{III}salen(H_2O)_2]Cl$, the Cr–O2 and Cr–O2′ distances of 1.806 and 1.811 in IIc are significantly shorter than those (1.916 and 1.951 Å) found in the chromium(III) complex.

Since cis coordination is known to occur in some metal–salen complexes,[44] we deemed it important to establish the molecular

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(38) Unfortunately, this study could not be carried out under rigorously anhydrous conditions since water cannot be removed from $Et_4NF{\cdot}2H_2O$ without forming the bifluoride ion.

(39) The amount of water introduced with the fluoride[38] is too small to cause this color change (compare Table VI).

(40) For example, we are unable to explain all the experimental data in a self-consistent way by postulating the formation of either a tight ion pair, a hypofluorite, or a salen adduct. Alternatively, the postulation of the second species as a difluoride adduct also poses some difficult problems. For peculiarities of fluoride association with iron porphyrins, see: Jones, J. G.; Tondreau, G. A.; Edwards, J. O.; Sweigart, D. A. *Inorg. Chem.* **1985**, *24*, 296.

(41) It is interesting to note that the gross coordination about Cr in O═Cr(salen)$^+$ is quite akin to the oxochromate(V) complex isolated by Roček and co-workers.[35]

(42) Gahan, B.; Garner, D. C., Hill, L. H.; Mabbs, F. E.; Hargrave, K. D.; McPhail, A. T. *J. Chem. Soc. Dalton Trans.* **1977**, 1726.

(43) For structural studies of salen–metal complexes, see: Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385.

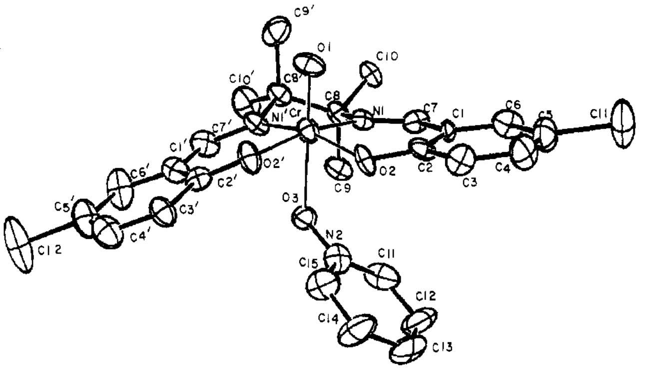

Figure 7. ORTEP diagram of the adduct of the oxochromium(V) cation from IIf with pyridine *N*-oxide.

Table VIII. Comparison of the Principal Structural Parameters of the Oxochromium(V) Cation and the Oxochromium(V)–Pyridine *N*-Oxide Adduct[a]

	$O{=}CrL^+$	$O{=}CrL'(pyO)^+$
	Bond Distances (Å)	
Cr–O1	1.545 (2)	1.554 (4)
Cr–O2	1.806 (2)	1.845 (5)
Cr–O2′	1.811 (2)	1.842 (5)
Cr–N1	1.969 (2)	2.017 (6)
Cr–N1′	1.991 (2)	1.960 (6)
Cr–O3		2.175 (5)
O3–N2		1.342 (8)
	Bond Angles (deg)	
O1–Cr–O2	109.10 (9)	100.1 (2)
O1–Cr–O2′	109.14 (9)	99.6 (2)
O2–Cr–O2′	84.63 (7)	89.5 (2)
O1–Cr–N1	105.08 (9)	93.8 (3)
O1–Cr–N1′	102.06 (9)	97.4 (3)
N1–Cr–O2	87.59 (8)	93.5 (3)
N1–Cr–O2′	145.60 (9)	165.6 (2)
N1–Cr–O2′	87.94 (8)	93.5 (3)
N1–Cr–O2	148.71 (8)	161.5 (2)
Cr–O3–N2		117.8 (4)
O1–Cr–O3		174.6 (2)

[a] Atoms identified as follows: O1 (oxo); O2, O2′ (salen); N1, N1′ (salen); O3, N3 (pyO). L = 7,7′-Me$_2$salen, L′ = 5,5′-Cl$_2$-8,8,8′,8′-Me$_4$salen. Numbers in parenthesis refer to the standard deviation in the last digit.

structure of the pyridine oxide adduct to the 5-coordinate [*N*,*N*′-ethylenebis(salicylidineaminato)]oxochromium(V) cations. The ORTEP diagram in Figure 7 shows that the coordination of the donor ligand occurs at the empty axial position to complete the octahedral coordination of chromium. The salen ligand maintains its essentially planar structure in the adduct. There are several important features of the adduct structure which merit discussion. Thus the O=Cr bond length increases by only 0.01 Å upon ligation—less than three standard deviations (see Table VIII). Nevertheless, the shift of ~60 cm^{-1} to lower energy of the IR stretching frequency $\nu_{O=Cr}$ indicates significant bond weakening upon axial coordination. Furthermore, the chromium atom is pulled back by 0.27 Å upon axial ligation—being only 0.259 (1) Å above the ligand plane in the pyridine oxide adduct. Similarly there is an elongation of the equatorial bonds to the salen oxygens (O2 and O2′) by 0.04 Å, which results in increase in the ligand bite [as measured by the nonbonded oxygen–oxygen (O2–O2′) bond distance in the salen ligand] from 2.44 to 2.60 Å. The long Cr–Opy bond of 2.18 Å probably reflects the high trans influence of the oxo ligand.[45] The remaining bond lengths and angles within the axial donor ligand are typical of other pyridine *N*-oxide complexes.[46] Note the N–O bond of the pyridine *N*-oxide eclipses the O=Cr bond with a torsional angle of only 2.5°. Although the cause of the asymmetry is unclear, the location of the pyridinyl ring away from the ethylene bridge undoubtedly reflects steric hindrance from at least one (axial) methyl substituent. Other minor structural differences between the (salen)oxochromium(V) cation and its pyridine oxide adduct include those of the salen moiety itself. The torsional angles at the ethylene bridge are 42.4 and 36.6° for the 5- and 6-coordinate complexes, respectively. This difference is accompanied by a decrease in the dihedral angle between the phenyl planes from 21.4 to 15.5° in the flattened half-chair conformation characteristic of these salen complexes.[43]

Table IX. Cyclic Voltammetry of O=CrL$^+$ Cations[a]

L	solvent	v, V s^{-1}	$E_{p,c}$,[b] V	ΔE_p,[c] V	$E_{1/2}$,[d] V
salen (IIa)	CH_3CN	0.50	0.42	0.010	0.47
	$(CH_3)_2SO$	0.50	0.31	0.08	0.37
5,5′-Cl$_2$salen (IIb)	CH_3CN	0.10	0.67	0.10	0.72
7,7′-Me$_2$salen (IIc)	CH_3CN	0.50	0.28	0.17	0.37
8,8,8′,8′-Me$_4$salen (IIe)	CH_3CN	0.50	0.59	0.090	0.63

[a] At 25 °C with 10^{-3} M oxochromium(V) and 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. [b] Cathodic peak potential. [c] Separation of cathodic and anodic peak potentials at the scan rate v indicated. [d] $(E_{p,c} + E_{p,a})/2$.

The closest interionic contact in the oxochromium(V) complex IIc is the O6···H5 distance of 2.69 Å. In the pyridine *N*-oxide adduct of the oxochromium(V) IIf the corresponding distance O4···H7 is 2.37 Å. These distances reveal that the triflate anion serves merely as an innocent counterion in both of the complexes.

V. Reduction of Oxochromium(V) Cations. Oxochromium(V) cations undergo a well-defined reduction, as judged by cyclic voltammetric (CV) studies at a platinum electrode. The cyclic voltammogram of the oxochromium(V) cation in dimethyl sulfoxide solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte is quasi-reversible, as indicated by the peak-to-peak separation of >80 mV at a scan rate of 1 V s^{-1} and the ratio of the cathodic and anodic peak currents of 1.8. Calibration with a ferrocene standard indicated the initial cathodic wave to correspond to a 1-electron reduction of oxochromium(V), i.e.

$$O{=}Cr(salen)^+ + e^- \rightarrow O{=}Cr(salen) \qquad (10)$$

However, the cathodic wave diminished upon repetitive CV scans, indicative of the gradual disappearance of the oxochromium cation. The reductive degradation of oxochromium(V) is also readily apparent by the shape of the CV wave in acetonitrile solutions. The large anodic current observed on the reverse scan is symptomatic of electrode pollution. Electrode deposition occurs in the form of a brown deposit. The similar brown precipitate that is formed during the chemical reduction of the oxochromium(V) cation IIa or IIc with ferrocene ($E°$ = 0.31 V) vs. SCE is tentatively ascribed to a neutral chromium(IV) derivative. We thus attribute the cyclic voltammetric behavior of oxochromium(V) to the transient character of these reduced species.

The average of the cathodic and anodic peak potentials in the cyclic voltammogram is a measure of the reduction potential of the oxochromium(V) cation,[47] and it is listed as $E_{1/2}$ in Table IX. The trend in the values of $E_{1/2}$ reflects the importance of the electronic effects of substituents, especially with regard to their location on the salen ligand.[48]

The reduction of oxochromium(V) is chemically effected by various donor ligands such as pyridines and phosphines. For example, the dark green-black color of oxochromium(V) is bleached immediately upon the addition of triethylphosphine. The

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(44) See: Hobday, M. D.; Smith, T. D. *Coord. Chem. Rev.* **1972**, *9*, 311. Calligaris, M.; Mangini, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1972**, 543.

(45) Hazell, A. C. *J. Chem. Soc.* **1963**, 5745.

(46) (a) Johnson, D. R.; Watson, W. H. *Inorg. Chem.* **1971**, *10*, 1068. (b) Horrocks, W. D. Jr.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1968**, *7*, 1552.

(47) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980.

(48) For an example of well-behaved redox behavior of an oxochromium(V) complex, see ref 31.

infrared and visible absorption spectra of the resulting light orange solution are the same as those obtained from the inner-sphere complex of (salen)Cr^{III} with triethylphosphine oxide. [The latter was synthesized directly from (salen)$Cr(OH_2)_2^+$ and excess triethylphosphine oxide and showed a characteristic metal-coordinated (P=OCr) stretching band at 1085 cm^{-1} (note in free Et_3PO, $\nu_{P=O}$ = 1135 cm^{-1}) in the infrared spectrum and an absorption band at λ_{max} = 395 nm for (salen)Cr^{III} in the UV–visible spectrum.] We thus conclude that the coordination of phosphine is either accompanied by or rapidly followed by oxygen atom transfer so that the overall transformation is

$$O{=}Cr^{V}L^+ + Ph_3P \rightarrow (Ph_3PO)Cr^{III}L^+ \qquad (11)$$

A coordinated intermediate can be observed as a transient green species when a large excess of pyridine is added to oxochromium(V), but it is rapidly converted to an orange complex, which we assign to the pyridine oxide adduct

$$O{=}Cr^{V}L^+ + py \rightleftharpoons O{=}Cr^{V}L(py)^+ \rightarrow (pyO)Cr^{III}L^+ \qquad (12)$$

Acknowledgment. We thank E. G. Samsel for the synthesis of the pyridine *N*-oxide adduct of IIf, J. D. Korp for the crystallographic structures in Figures 6 and 7, and the National Science Foundation and the R. A. Welch Foundation for financial support.

Supplementary Material Available: Tables of all bond distances, torsional and bond angles, anisotropic temperature factors, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 75. Reduction of Carboxylato-Bound Chromium(V) with Vanadium(IV). Intervention of Chromium(IV)[1]

Y.-T. Fanchiang, Rathindra N. Bose,*† E. Gelerinter, and E. S. Gould*

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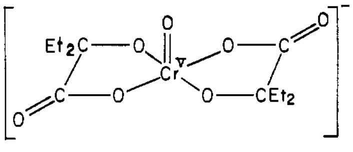
The chelated (carboxylato)chromium(V) anion bis(2-hydroxy-2-ethylbutyrato)oxochromate(V) (I), $[(Lig)_2Cr(O)]^-$, reacts with oxovanadium(IV) to form a strongly absorbing species (λ_{max} = 515 nm; $\epsilon = 1.7 \times 10^3$ M^{-1} cm^{-1}) in the presence of 2-hydroxy-2-ethylbutyric acid buffers (pH 2–4). EPR data support 1:1 stoichiometry with VO^{2+} in deficiency, indicating the formation of a chromium(IV) species by a 1e reduction process. With excess VO^{2+} a chromium(III) product corresponding to a 2e reduction process was obtained. Spectral and ion-exchange properties of this product correspond to those observed for the titanium(III) and iron(II) reductions of chromium(V) and are consistent with the formulation of the product as a bis(hydroxycarboxylato) chelate of $(H_2O)_2Cr^{III}$. With excess vanadium(IV), the reaction exhibits triphasic kinetics. Two components of the triphasic profile are attributed to the parallel formation of chromium(IV) species from a slowly equilibrating ligation process: $(Lig)_2Cr(O)^- + Lig^- \rightleftharpoons (Lig)_3Cr(O)^{2-}$. The equilibrium constant, 51 ± 7 M^{-1} for this process, evaluated spectrophotometrically, was consistent with the values 46 and 64 M^{-1} generated from the kinetic profile. The remaining step of the reaction is the reduction of the chromium(IV) intermediate with VO^{2+}. Rates for all three steps increase with decreasing $[H^+]$ and level off at low $[H^+]$. The limiting rate constants for the formation of the chromium(IV) intermediate by the $(Lig)_3Cr(O)^{2-}$ and $(Lig)_2Cr(O)^-$ pathways are 2.8×10^3 and 2.2×10^2 M^{-1} s^{-1}. The bimolecular limiting rate constant for the reduction of chromium(IV) is computed to be 7.7×10^2 M^{-1} s^{-1}. Like the iron(II)–chromium(V) redox couple, the vanadium(IV) reduction of Cr(V) is taken to be an inner-sphere process.

The facile synthesis of water-soluble complexes of chromium(V), reported in 1979,[2] made available an additional unusual oxidation state to workers dealing in electron-transfer processes. Of particular interest are the reactions of Cr(V) with 1e reductants, for these must, in principle, proceed through the even rarer oxidation state chromium(IV). Although the reactivity of the latter has thus far precluded its detection in reactions of Cr(V) with Ce(III)[3] and Ti(III),[4] a transient species having properties corresponding to a complex of Cr(IV) was detected in reductions of Cr(V) chelate I with Fe(II).[5] In the present study, which pertains to the reaction of VO^{2+} with chelate I, we find evidence for intervention of the same, or a closely related, transient. The system at hand appears to be somewhat more complex than the earlier Cr(IV)–Fe(II) reaction, but it is more amenable to examination with ESR spectroscopy.



I

Experimental Section

Materials. Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (complex I) was prepared as its monohydrate as described;[2] good-quality crystals of this complex were obtained by dissolving the complex in acetone at room temperature, gradually adding chloroform to incipient crystallization, and then slowly cooling to 0 °C. This chelate was kept in the dark at 0 °C. Aqueous solutions of the complex exhibited a maximum at 510 nm with an extinction coefficient of 161 M^{-1} cm^{-1} (lit.[2] 168 M^{-1} cm^{-1}); this value rose to 189 M^{-1} cm^{-1} in the presence of a large excess of carboxylato ligand, reflecting a ligation equilibrium (see below).[6] Solutions of $VO(ClO_4)_2$ were prepared by treating $VOSO_4$ (Alfa) with an equivalent quantity of $Ba(ClO_4)_2$ and then removing the precipitated $BaSO_4$.[7] Concentrated vanadyl solutions could be analyzed spectrophotometrically for VO^{2+} in 1 M $HClO_4$ (ϵ_{760} = 17.2 M^{-1} cm^{-1}),[8] whereas more dilute solutions were analyzed as the hydroperoxy complex as described.[9] Solutions of $Eu(ClO_4)_2$ were prepared by the method of Fan.[10] Lithium perchlorate, for use in kinetic experiments, was prepared by the method of Dockal[11] and recrystallized twice before use. Cation-

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† Present address: Chemistry Department, Pittsburg State University, Pittsburg, KS 66762.

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(2) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

(3) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

(4) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.

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(6) Aqueous solutions of Cr(V) chelate I, if stabilized by 0.05 M 2-ethyl-2-hydroxybutyric acid at pH 3, decompose only slowly in the dark but undergo rapid decomposition to Cr(III) species in direct sunlight.

(7) This precipitation is best carried out by adding a slight excess of $Ba(ClO_4)_2$ solution to aqueous $VOSO_4$, removing the precipitated $BaSO_4$ by centrifugation (rather than by filtration), adding additional $VOSO_4$ dropwise until no further precipitate forms, cooling to 0 °C, and then centrifuging once more.

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