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Isolation and Molecular Structure of Unusual Oxochromium(v) Cations for the Catalytic Epoxidation of Alkenes

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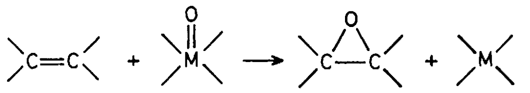
The first *X*-ray crystal structure of an oxochromium(v) complex capable of effecting oxygen atom transfer to alkenes in stoicheiometric and catalytic systems is reported.

Oxygen atom transfer to effect the catalytic epoxidation of alkenes with oxometal species, *i.e.*, equation (1), is currently of synthetic and theoretical interest.[1–4] We report the first isolation and structure determination of a series of catalytically active oxochromium(v) complexes generated from various well-characterized chromium(III)salen [salen = *N,N'*-ethylenebis(salicylideneaminato)] complexes.[5] In a typical example, the treatment of $\mathrm{Cr(salen)(H_2O)_2{}^+PF_6{}^-}$ with iodosylbenzene in acetonitrile, followed a few minutes later by the slow addition of diethyl ether, led to the isolation of $\mathrm{O{=}Cr(salen)^+PF_6{}^-}$ (**1**) in 87% yield [equation (2)]. Careful recrystallization of the oxochromium(v) salt from an equimolar mixture of acetonitrile and chlorobenzene afforded dark brown crystals of sufficient quality for *X*-ray crystallographic determination.† The molecular structure of the oxochromium(v)salen cation shown in Figure 1 bears an interesting relationship to that of its chromium(III) precursor, the structure of which was determined earlier by Coggon and coworkers.[5] Indeed the planar salen ligand is essentially the same in both cations [see Figure 1(a)]. However upon oxygen atom transfer, the chromium(v) centre in (**1**) is displaced *ca.* 0.5 Å above the salen plane to describe a roughly square pyramidal arrangement [see Figure 1(b)].‡



(1)

$$\mathrm{Cr^{III}(salen)(H_2O)_2{}^+PF_6{}^-} + \mathrm{PhIO} \xrightarrow{-\mathrm{H_2O}} \mathrm{O{=}Cr^{V}(salen)^+PF_6{}^-}\ (\mathbf{1}) + \mathrm{PhI} \qquad (2)$$

The analogous halogen derivatives of oxochromium(v)salen could be readily prepared from a solution of (**1**) by the addition of the appropriate tetra-alkylammonium halide. In each case, the electronic spectrum is characterized by a broad, long-wavelength absorption band as listed in Table 1. The prominent feature of the i.r. spectra of the oxochromium(v) complexes is a strong absorption band assigned to the O=Cr stretch (see Table 1).[7] The isotropic e.s.r. spectrum of the paramagnetic oxochromium(v)salen cation (**1**) centred at $\langle g \rangle = 1.977$ in Figure 2 shows the well-resolved quintet splitting arising from the two equivalent nitrogen atoms in the salen ligand with $a(^{14}\mathrm{N}) = 2.25$ G (1 G = 10^{-4} T).[7,8] Furthermore, the weaker lines of the spectrum are clearly associated with the 4 sets of lines arising from the ^{53}Cr isotopic ($I = 3/2$, 9.54% natural abundance) splitting of 18.9 G.

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† *Crystal data* for compound (**1**), space group *C2cm*, $Z = 4$, $a = 6.540(4)$, $b = 20.573(10)$, $c = 15.164(9)$ Å at −160 °C. An unco-ordinated MeCN and $\mathrm{PF_6{}^-}$ also lie in the cell with closest contacts greater than 3.0 Å. The structure was disordered with oxochromium sites on either side of the salen plane, and their relative occupancies converged to 60:40 as a result of full matrix refinement. The major component shown in Figure 1 consists of Cr lying 0.59(6) Å above the plane with a Cr–O distance of 1.49(4) Å. In the minor component, the Cr lies 0.45(6) Å below the salen plane with a Cr–O distance of 1.62(5) Å. Neither the Cr–O distances nor the out-of-plane displacements differ significantly in the two components, and the averages, Cr–O 1.56(5) Å, and displacement 0.52(5) Å should be taken as the best estimates for these parameters. In addition there is disorder at C(12), with the C(12)–C(12′) distance varying from 1.30(2) to 1.39(5) Å depending on which disordered pair was chosen. Final residuals for 1225 observed (out of 1661 unique) intensities (Mo-K_α for $6 \leqslant 2\theta \leqslant 50°$) are $R = 0.097$ and $R_w = 0.077$. The vectors from a 3-dimensional Patterson plot showed a distinct Cr–Cr′ peak consistent with the disordered model. Examination of the packing in the unit cell revealed the Cr–O vectors to be aligned and parallel to the *a* axis which suggests that the disorder is only 2 dimensional. The extreme difficulty we encountered in growing the crystal suitable for crystallographic study reflects the disorder described above and the relatively high residuals. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Similar structures have been observed in an anionic oxochromium(v)bis(α-hydroxybutyrate) and in a neutral oxochromium(IV)porphyrin (ref. 6).

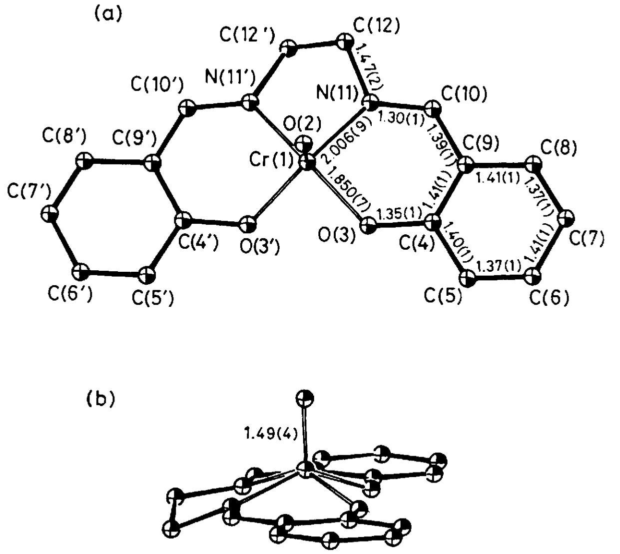


Figure 1. The structure of the oxochromium(v)salen cation from the top (a) and side (b) perspectives with some important distances (Å). A mirror plane lies perpendicular to the plane of the salen ligand with a disorder in the position for C(12). The Cr–O moiety is also disordered with the minor component lying below the salen plane.†

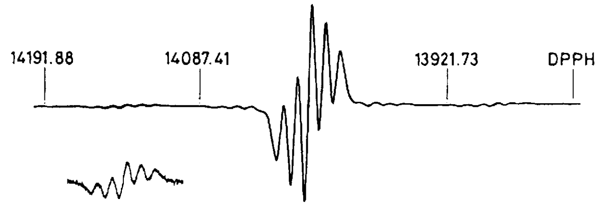


Figure 2. Isotropic e.s.r. spectrum of 5×10^{-4} M oxochromium(v)-salen (**1**) in acetonitrile solution at 25 °C. The inset shows the $M_I = 3/2$ line for ^{53}Cr at higher gain (× 10). The proton n.m.r. field markers are in kHz. DPPH = diphenylpicrylhydrazyl.

Table 1. Spectral properties of oxochromium(v)salen complexes.

O=Cr(salen)X X	$\lambda(\epsilon)_{max}$/ nm (dm^3 mol^{-1} cm^{-1})^a	ν(O=Cr^V)/ cm$^{-1\,b}$	$<g>^a$
Hexafluorophosphate	575 (1550)	997	1.97(7)
Fluoride	614 (2290)	935	1.97(3)
Chloride	644 (2490)	950	1.97(7)
Bromide		953	

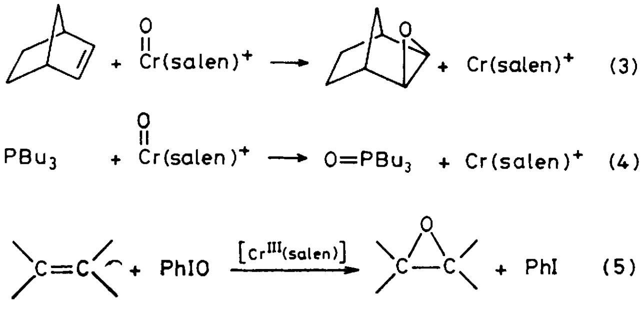
^{a} Acetonitrile solution. ^{b} Nujol mull.

It is noteworthy that the oxochromium(v)salen complexes are capable of efficient oxygen atom transfer to alkenes as well as phosphines, *e.g.* equations (3) and (4) . Such facile oxygen atom transfers, coupled with the ease by which oxochromium(v) species can be generated from the corresponding chromium(III) complex [equation (2)], allow catalytic systems to be developed with chromiumsalen complexes. For example, we have successfully carried out the epoxidation of the various alkenes listed in Table 2 with iodosylbenzene in the presence of catalytic amounts of chromium(III)salen, *i.e.* equation (5). No reaction occurred in the absence of the chromium complex.

Table 2. Chromium-catalysed epoxidation of alkenes with iodosylbenzene.^{a}

Alkene	Epoxide/ 10^2 mmol (%)^b
Norbornene	13.6 (82)
Cyclo-octene	7.9 (41)
Tetramethylethylene	9.8 (61)
Styrene	4.0 (24)
β-Methylstyrene	9.8 (59)
2,3-Dimethylbutadiene	10.4 (62)^c
Oct-2-ene	3.0 (18)
Cyclohexene	<0.5 ^{d}
Methylcyclohexene	1.4 (8)
Hex-1-ene	<0.5

^{a} Alkene (4.8 mmol) and iodosylbenzene (0.16 mmol) treated with 2.5×10^{-2} mmol Cr(salen)(H$_2$O)$_2$PF$_6$ in 1 ml CH$_2$Cl$_2$ containing 7.5×10^{-2} mmol pyridine. Reactions carried out at ambient temperatures until complete conversion into iodobenzene. ^{b} Yields based on iodosylbenzene charged. ^{c} Monoepoxide. ^{d} Cyclohex-2-enol and cyclohex-2-enone are principal products.



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