Summary

The triply bridged complex I constitutes an unusual example of a compound having an enforced geometry that allows for the demonstration of a significant and experimentally measurable degree of pure electrostatic interaction. Typically, because of the requirement of saturated linkages to prevent through-bond charge delocalization, such interactions are not observable. Both the synthesis and electrochemistry of this dinuclear complex are semiquantitatively explainable in terms of simple electrostatics. Finally, the behavior of the Fe complex is not unique; the general features reported here appear to extend to other isostructural complexes, as well.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE 8516904) for generous support of this work. The Nicolet R3m diffractometer and computing system were purchased with funds provided by the National Science Foundation (Grant No. CHE 8103011). We also thank J. Osteryoung and J. O'Dea for analyzing the OSWV data.

Registry No. I^{6+}, 117251-64-6; I^{5+}, 117251-65-7; I^{3+}, 117251-66-8; I^{2+}, 117251-67-9; I^{+}, 117251-68-0; I, 117251-69-1; I^{-}, 117251-70-4; I^{2-}, 117251-71-5; $I(CF_3SO_3)_4$, 117251-61-3; $I(ClO_4)_4$, 117251-58-8; $I(PF_6)_4$, 117251-59-9; II^{3+}, 34032-03-6; II^{+}, 71619-84-6; II, 20515-12-2; II^{-}, 71619-85-7; $II(PF_6)_2$, 85185-57-5; III, 117251-63-5; $Ru(bpy)_2Cl_2$, 15746-57-3.

Supplementary Material Available: Tables of crystallographic details, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom parameters for I (11 pages); a table of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Departments of Inorganic
and Physical Chemistry, University of Melbourne,
Parkville, Victoria 3052, Australia

Electronic Spectra of the Solvated Cations of Chromium(III) and Manganese(II) in Anhydrous Hydrogen Fluoride

Colin G. Barraclough,* Russell W. Cockman,
Thomas A. O'Donnell,* and Margaret J. Snare

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Previous work from this laboratory has shown that whereas transition-metal difluorides and trifluorides have very low solubilities in anhydrous hydrogen fluoride (AHF), solutions of transition-metal cations in AHF can be prepared by reaction of a transition metal or its fluoride with AHF, the acidity of which has been enhanced deliberately by addition of an appropriate Lewis acid such as BF_3, AsF_5, or SbF_5. UV-visible and Raman spectra of many such solutions have been reported.[1-4]

The previous electronic spectra were interpreted in crystal field terms, with the perturbing field assumed to be due to coordinated HF molecules. The present work extends the range of ions to include Cr^{3+} and Mn^{2+}. ESR spectra of these ions in AHF have also been observed.

Experimental Procedures

Vacuum Manipulation. Volatile fluorides were transferred individually in a stainless-steel vacuum system, based on stainless-steel Swagelok unions and Whitey valves (SS-1KS4), to Kel-F reaction tubes fitted with Kel-F valves for preparation of solutions for spectroscopy. The passivating metal fluoride layer is dissolved if HF and a Lewis acid are in the metal section of the vacuum system simultaneously. However Kel-F is resistant to HF solutions of Lewis acids. High pressures of volatile compounds were measured with Bourdon gauges and pressures in the millitorr range with a Varian 801 thermocouple gauge.

Reagents. AHF. Commercially available HF (Matheson, 99.8%) was purified by four trap-to-trap distillations in a well-conditioned Kel-F apparatus, using $CaCl_2$–H_2O–dry ice as the coolant for condensation at −45 °C and discarding "heads and tails". Purity was checked by measurement of electrical conductance, the value typically being $1 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 0 °C.

F_2 and AsF_5. F_2 (Matheson) and AsF_5 (Ozark-Mahoning) were used as received.

SbF_5. The purification procedure previously reported[5] was followed, with collection of the fraction boiling in the range 143–145 °C. Since SbF_5 was effectively involatile at the vacuum line pressures used during this work, the reagent was manipulated in the form of solutions in AHF, typically approximately 5 M.

Metals. Mn (Koch Light, 99.5%) and Cr (Koch Light 99.4%) were used as massive metal, rather than powders, in order to minimize contamination by surface oxides. Surface oxide was removed as reported earlier.[4]

Preparation of Solutions. $(NH_4)_3CrF_6$. The solid fluorochromate was prepared according to the method of Sturm.[6] Solutions of the solid in "neutral" AHF were not entirely stable, precipitation of CrF_3 occurring on standing. Stable green solutions were obtained by using a large excess of fluoride, typically 5 M in NH_4F.

$Mn(AsF_6)_2$. In a typical run, 0.55 g of cleaned metallic Mn was weighed into a Kel-F tube. After evacuation, AHF (20 cm^3) was distilled in and excess AsF_5 (measured by *PVT* relationships) was added at −196 °C. The contents were allowed to warm to ambient temperature, and initiation of reaction was indicated by the evolution of a gas not condensable at −196 °C, hydrogen. After the mixture was allowed to stand overnight, the metal had dissolved, forming a clear colorless solution, which was solidified by cooling, and the quantity of H_2 formed was measured. This was never found to be as required by eq i because some of the excess AsF_5 acted as an oxidant according to eq ii. The presence

$$Mn + 2HF + 2AsF_5 \rightarrow Mn_{solv}{}^{2+} + H_2 + 2AsF_6{}^- \qquad (i)$$

$$Mn + 3AsF_5 \xrightarrow{HF} Mn_{solv}{}^{2+} + AsF_3 + 2AsF_6{}^- \qquad (ii)$$

of the AsF_3 impurity was found to have no detrimental effect on the subsequent spectroscopic studies reported here.

For analysis, a known volume of the solution of Mn^{2+} in AHF was dissolved in water and oxidized to MnO_4^-, which was determined spectrophotometrically at 525 nm.

$Cr(SbF_6)_3$. Massive crystalline chromium (0.04 g) was weighed into a Kel-F tube, which was evacuated. A 6 M solution of SbF_5 in AHF (5 cm^3) was introduced into the evacuated tube, and reaction was allowed to occur at ambient temperature. After several hours the metal had dissolved, leaving a pale green-blue solution, which was shown by UV-visible spectroscopy[2] to contain $Cr_{solv}{}^{2+}$. As noted above the stoichiometric quantity of hydrogen expected from eq iii was not observed, indicating that some of the SbF_5 had been reduced during the reaction (see eq ii).

$$Cr + 2HF + 2SbF_5 \xrightarrow{HF} Cr_{solv}{}^{2+} + H_2 + 2SbF_6{}^- \qquad (iii)$$

Caution! For the subsequent step it is imperative that all of the liberated hydrogen is removed by repeatedly freezing the solution and pumping off H_2. Fluorine, in a small excess over that required to convert Cr(II) to Cr(III) by eq iv, was added at −196 °C, and the reaction was

$$2Cr_{solv}{}^{2+} + F_2 + 2SbF_5 \rightarrow 2Cr_{solv}{}^{3+} + 2SbF_6{}^- \qquad (iv)$$

allowed to proceed as the solution warmed to ambient temperature. If

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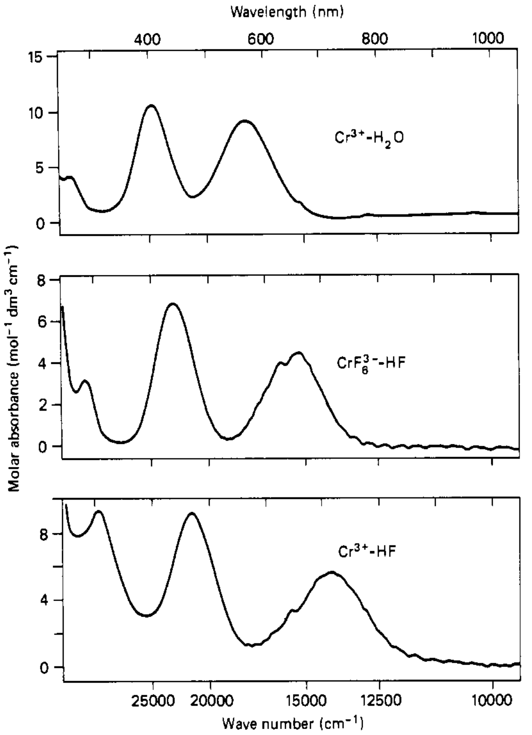

Figure 1. UV-visible spectra of Cr(III) as $Cr(OH_2)_6^{3+}$ in H_2O, CrF_6^{3-} in HF, and $Cr(FH)_6^{3+}$ in HF.

the tube was left undisturbed, the characteristic yellow-green of Cr^{III} could be seen to develop at the gas-liquid interface as the reaction proceeded. When the mixture was shaken for a few minutes, all the Cr(II) was oxidized, as indicated by spectroscopy, and a clear yellow-green solution with a trace of insoluble green precipitate remained. Excess fluorine was removed by pumping at −196 °C. The small quantity of CrF_3 was removed by using the Teflon and Kel-F filter cartridge previously described.[2]

It is important to note that best results were obtained when a large excess of the strong Lewis acid (typically 30:1) was used. At lower ratios the amount of insoluble precipitate increased leading to a correspondingly lower yield of Cr_{solv}^{3+} in solution. When, in the extreme case, the oxidation was carried out in the presence of an excess of a weak Lewis acid, such as BF_3, all of the chromium was precipitated as insoluble green CrF_3.

However, the Cr(III) solutions were found to be stable indefinitely when prepared as above with the necessary large excess of strong Lewis acid.

For spectroscopic studies the Cr concentration (0.14 M) was determined by addition of a known volume of HF solution to the aqueous solution and oxidation to $Cr_2O_7^{2-}$, followed by titration against Fe^{2+}.

Spectral Cells and Recording of Spectra. A pair of Kel-F-bodied spectral cells with synthetic sapphire windows and path lengths of 0.67 cm was used for recording Cr(III) spectra. They were constructed as described previously.[1] For the Mn(II) spectra, with weaker absorptions, two cells of longer path lengths (10.25 cm) were constructed in similar fashion.

A distinct ESR spectrum for Mn^{2+} in AHF was obtained in a Kel-F tube (0.25-in. o.d.) because of the strength of the signal. However this simple cell was found to be unsatisfactory for Cr^{3+}. A new cell, similar to the small path length cells used for aqueous work, was made from Kel-F tubing (0.25-in. o.d) with the central section flattened by compression at 100 °C between parallel clamped plates to provide a cavity approximately 0.02 in. in width. The ends of the tubing were flared. The lower end was sealed by a tapered Kel-F plug connected by brass nuts, and the upper flare was attached directly to a standard Kel-F valve by another nut.

A disadvantage of this cell was that highly accurate g values could not be obtained because of the inability to simultaneously insert a pitch sample, required for calibration, in the magnetic field. For analysis of the Cr(III) solution it was adequate to use the known g value of an included manganese(II) impurity in the necessary calculation.

In this work, Raman spectra were recorded for solutions contained in synthetic sapphire tubes (0.25-in. o.d.) capped with a Kel-F valve.

Instruments used for recording UV-visible, ESR, and Raman spectra respectively were a Cary 17, a Varian V4502-15 and a Spex Ramalog, Model 14018, with argon ion laser excitation (5145 Å).

Table I. Spectral Data for Cr(III) Systems (Ground State $^4A_{2g}$)

upper state	$Cr(FH)_6^{3+}$ [a] E, cm^{-1} calcd	exptl	CrF_6^{3-} [b] E, cm^{-1} calcd	exptl
$^4T_{2g}$	14 000	14 000	14 900	14 900
^2E_g	15 600	15 500	15 700	15 700
$^2T_{1g}$	16 300	16 300		
$^4T_{1g}$(F)	21 000	21 000	22 300	22 300
$^4T_{1g}$(P)	32 600	32 500	34 700	34 600

[a] Postulated entity for solvated Cr(III) in acidic AHF. [b] In basic AHF.

Table II. Ligand Field Parameters for Cr(III) Systems in Octahedral Environments

complex	C/B	Δ/B	B	C	Δ	ref
$Cr(FH)_6^{3+}$	4.4	18.3	767	3370	14 030	*a*
CrF_6^{3-}(AHF, aq)[b]	4.1	18.5	808	3310	14 950	*a*
CrF_6^{3-}(aq)	4.0		900			
			820		15 200	8
K_2NaCrF_6(solid)	4.0	21.2	760	3020	16 100	12
CrF_3(solid)			740		14 600	12
$Cr(OH_2)_6^{3+}$(aq)	4.2	22.6	754	3170	17 040	*a*
	4.0		835			
			725		17 390	8
free ion	4.1		830	3430		12
	4.0		920	3680		13

[a] Although the value of B derived from a spin-allowed transition will, in general, be different from that derived from a spin-forbidden one, an average value was used in these calculations. [b] Spectra recorded for CrF_6^{3-} in AHF and in H_2O in present work.

Table III. ESR Line Widths for Cr(III) Complexes

complex	solution	line width, G	g	ζ	ref
$Cr(FH)_6^{3+}$	0.1 M $Cr(SbF_6)_3$ in acidic AHF	224	1.98	105	*a*
CrF_6^{3-}	0.5 M $(NH_4)_3CrF_6$ in basic AHF	65	1.95	280	*a*
CrF_6^{3-}	0.1 M $(NH_4)_3CrF_6$ in H_2O	80			9
$Cr(OH_2)_6^{3+}$	0.1 M $Cr(ClO_4)_3{\cdot}6H_2O$ in H_2O	222	1.98	128	9
Cr^{3+}	0.1 M $Cr(ClO_4)_3{\cdot}6H_2O$ in acetone	146			*a*

[a] This work.

Results and Discussion

Chromium. The absorption spectra in the visible and near-UV region for Cr^{3+} in AHF, CrF_6^{3-} in AHF, and Cr^{3+} in water are shown in Figure 1. Band positions and assignments made on the basis of octahedral coordination are given in Table I. The crystal field theory for octahedral d^3 ions is well-known,[7] and the crystal field parameters for our systems and some related compounds are given in Table II. Band positions calculated from these parameters are given in Table I and show excellent agreement with the experimental band positions.

The relative intensities of the bands for Cr^{3+} in AHF and water show a similar pattern, but the absolute intensities of the bands in AHF are about half those in water. This reduction in intensity seems to be a general feature of coordination with HF and has been seen in all our previous work. The results in Table II for the crystal field splitting parameter Δ give the order $H_2O > F^- > HF$ for these ligands in the spectrochemical series.

The stability of the complex ion CrF_6^{3-} in both AHF and water proved advantageous. We recorded again the visible absorption spectrum of CrF_6^{3-} in water, which has been reported previously,[8] and it is identical within experimental error with our spectrum for CrF_6^{3-} in AHF. This supports the usual assumption that the second and subsequent coordination spheres have little effect on the crystal field spectra. $Cr(FH)_6^{3+}$ and CrF_6^{3-} can be regarded as providing the limits of the species exhibited by Cr(III) in acidic and basic HF, with solid CrF_3 the species expected in nearly

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Table IV. Spectral Data for Mn(II) Systems (Ground State $^6A_{1g}$)

	$Mn(FH)_6^{2+}$ [a]			MnF_2			$Mn(OH_2)_6^{2+}$		
	E, cm^{-1}			*E*, cm^{-1}			*E*, cm^{-1}		
upper state	calcd	exptl	ϵ	calcd	exptl[b]	ϵ^b	calcd	exptl[c]	ϵ^c
$^4T_{1g}(G)$	22 700	22 700	0.015	20 000	19 440	0.038	19 400	18 870	0.018
$^4T_{2g}(G)$	24 900	24 700	(0.01)	23 050	23 500 25 190	0.025	22 800	23 120 24 960	0.015
$^4A_{1g}$,$4E_g$(G)	25 600	25 800	0.095	24 680	25 300 25 500	0.15	25 200	25 275	0.038
$^4T_{2g}(D)$	30 800	30 800	(sh)	28 200	28 120 28 370	0.034	28 200	27 980	0.021
$^4E_g(D)$	29 800	29 800	0.024	29 760	30 230		29 900	29 750	0.022
$^4T_{1g}(P)$				33 380	33 060	0.06	35 000	32 960	0.015
$^4A_{2g}(F)$				40 350	39 000		40 700	40 820	
$^4T_{1g}(F)$	42 100	42 200	0.002	41 120	41 400				

[a] Postulated entity for Mn(II) in acidic AHF. [b] Reference 14. [c] Reference 15.

neutral HF. By variation of the acidity of the AHF solvent, it should be possible in principle to obtain various proportions of intermediate species such as $(Cr(FH)_5F)^{2+}$, $(Cr(FH)_4F_2)^+$ etc. This lowering in symmetry should lead to splitting and shifts of the bands in the spectra, but the shifts would be small, and we have not been able to observe any such splitting.

A single broad line is seen in the ESR spectra of Cr^{3+} and CrF_6^{3-} in AHF. The *g* values and the line widths for these species and the corresponding quantities in water are given in Table III. For d^3 systems the g value is given by

$$g = 2.00 - 8\zeta/2\Delta$$

where ζ is the spin–orbit coupling parameter. Using the Δ values from the electronic spectra, we can calculate values for ζ and these are also shown in Table III. As expected for coordinated ions, these ζ values are reduced compared to the free ion value of 273 cm^{-1} for Cr^{3+}. The *g* value and the derived ζ value for CrF_6^{3-} in AHF appear to be inconsistent with the rest of the data. As was pointed out in the Experimental Section, simultaneous calibration with a pitch sample was not possible and the value needs to be checked with a modified experimental configuration. McGarvey[9] has shown that the width of the ESR line depends on the distortion from perfect octahedral symmetry as measured by the zero-field splitting parameter *D* and the rotational correlation time.

The line width for $Cr(FH)_6^{3+}$ in AHF is very similar to that for $Cr(OH_2)_6^{3+}$ in water, but the two factors affecting the line width could have changed in opposite directions. It might be expected that rotational correlation times in HF would be shorter because the bulk viscosity of AHF is less than that of water. AHF has a viscosity of 0.25 cP at 0 °C compared with 1.0 cP for water at 20 °C. However rotational correlation times will also depend on the solute–solvent interactions as well as on the bulk viscosity, and in both solvents there will be strong hydrogen bonding between the solvated cations and the solvent. An example of the effect of viscosity on the line width of $Cr(OH_2)_6^{3+}$ is shown in Table III, where the line widths in water and acetone are compared. Acetone at 20 °C has a viscosity of 0.33 cP, i.e. one-third that of water, and the line width in acetone is 65% of that in water.

Manganese. The crystal field spectra for Mn^{2+} are very weak since the transitions are spin forbidden and in octahedral symmetry are Laporte forbidden. The visible absorption spectrum of Mn^{2+} in AHF can be easily observed, but unfortunately it is not as well resolved as that for Mn^{2+} in water. The band positions and assignments, assuming octahedral symmetry, are given in Table IV for Mn^{2+} in AHF and in water, and for Mn^{2+} in solid MnF_2. Again the intensities are less in AHF than in water, but because of the poor resolution in AHF the extinction values are only approximate.

The conventional crystal field theory[7] for high-spin d^5 systems in octahedral symmetry was used to calculate the parameters given in Table V and the band positions given in Table IV. There is good agreement for Mn^{2+} in AHF, but the agreement is not quite so good for Mn^{2+} in water and MnF_2. More elaborate theory[10a] has been used to provide a better fit for Mn^{2+} in water and in MnF_2 but does not seem to be necessary for Mn^{2+} in AHF. Again the Δ values are in the order $H_2O > F^- > HF$ as for Cr^{3+} and other cations studied earlier in this program.

Table V. Ligand Field Parameters for Mn^{II} Systems

complex	*C*/*B*	Δ/*B*	*B*	*C*	Δ	ref
$Mn(FH)_6^{2+}$	5.0	7.0	733	3663	5128	
MnF_2[a]	4.8	9.7	726	3484	7040	
	4.1	9.1	825	3346	7500	14
$Mn(OH_2)_6^{2+}$	5.1	12.1	708	3608	8562	
	5.5	12.6	671	3710	8480	15
	3.9	9.2	828	3243	7600	16
free ion	3.46		960	3325		17

[a] Fluoride ions are arranged at the corners of a distorted octahedron.

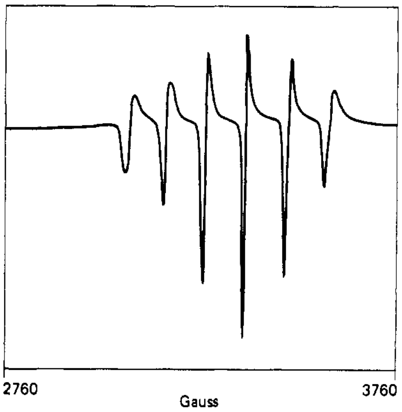

Figure 2. ESR spectrum for Mn(II) in HF.

The ESR spectrum for Mn^{2+} in AHF is shown in Figure 2. It is very similar to that of Mn^{2+} in water with the characteristic six lines due to hyperfine splitting with the nuclear spin on the manganese. The *g* value is 2.012 and the hyperfine splitting parameter *a* is 105 G (294 MHz). The lines are rather narrower than in the water. The theory of the line broadening for Mn^{2+} is closely related to that for Cr^{3+}, so it could be the lower viscosity of AHF or a smaller zero field splitting in $Mn(FH)_6^{2+}$ that produces the narrower lines.

Evidence for Coordination of HF to Cations. Although the crystal field spectra strongly support the proposition of octahedral coordination of HF molecules around the Cr^{3+} and Mn^{2+} cations, it is highly desirable to look for more direct evidence for coordinated HF. It has proved very difficult to isolate from AHF crystalline solids that are suitable for X-ray crystallographic structure determination and that contain HF molecules of sol-

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vation. A crystalline Mn(II) compound was isolated from HF acidified with BF_3, and it was hoped that it was $Mn(FH)_6(BF_4)_2$. In fact it proved to be the ansolvate $Mn(BF_4)_2$ in which seven-coordinate Mn^{2+} is bridged through terminal fluorine atoms of BF_4^- anions in an arrangement in which four of the BF_4^- anions bridge four Mn^{2+} atoms and the remaining three bridge to three Mn^{2+} atoms; i.e., the formula can be written as $Mn(BF_4)_{4/4}(BF_4)_{3/3}$.[10b]

Raman spectroscopy is a technique that could give further evidence for the presence of coordinated HF molecules. The Raman spectrum of Cr^{3+} in AHF did not show any bands that could be associated with Cr–F vibrations. Although disappointing, this is not very surprising. The Cr–F bonds will be fairly ionic in character, and would be expected to give very weak Raman spectra. An indication of the difficulty of detecting Cr–F vibrations can given by experiments on the CrF_6^{3-} ion. In AHF solution no Raman spectrum could be detected, but with a solid sample of $(NH_4)_3CrF_6$, a Raman band was observed at 543 cm^{-1}. This can be reasonably assigned as the totally symmetric A_{1g} Cr–F stretching mode, which is consistent with previous assignments of infrared bands at 535 and 522 cm^{-1} as Cr–F stretching modes.[11]

With Mn^{2+} in AHF, a broad band was observed at 545 cm^{-1} in the Raman spectrum of the most concentrated solution. It is not possible to be certain that this is a Mn–F stretching frequency, but it is in the expected region of the vibrational spectrum. The solid $Mn(BF_4)_2$ has a broad Raman band centered at 532 cm^{-1}, but there are two different types of Mn–F links in this compound and they could both be contributing to the observed band. Overall it can be said the Raman spectra give some evidence for HF coordination, but still more direct evidence is required.

Acknowledgment. Financial assistance from the Australian Research Grants Scheme for this work is gratefully acknowledged.

Registry No. $Cr(FH)_6^{3+}$, 117226-19-4; CrF_6^{3-}, 15276-04-7; $Cr(OH_2)_6^{3-}$, 15276-04-7; $Cr(OH_2)_6^{3+}$, 14873-01-9; Cr^{3+}, 16065-83-1; $Mn(FH)_6^{2+}$, 117226-20-7; MnF_2, 7782-64-1; $Mn(OH_2)_6^{2+}$, 15365-82-9; HF, 7664-39-3.

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Contribution from the Alchemie Research Centre,
P.O. Box No. 155, Thane Belapur Road,
Thane-400 601, Maharashtra, India

Effect of a Clay Support on the Catalytic Epoxidation Activity of a Manganese(III)-Schiff Base Complex

Prasad S. Dixit and K. Srinivasan*

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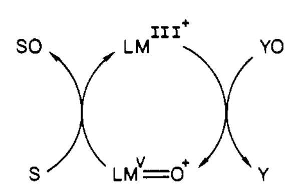
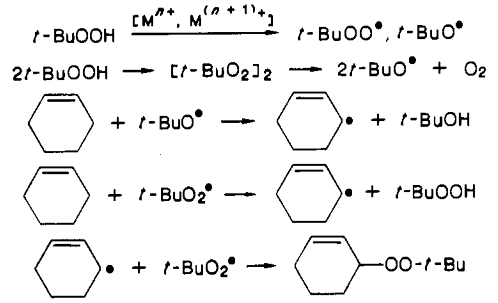
Manganese(III) complexes of porphyrin and Schiff base ligands have attracted considerable interest recently as catalytic oxygen transfer relays.[1,2] Scheme I illustrates the general epoxidation pathway in these systems involving oxidants such as iodosylbenzene,[3] hypochlorites,[4] *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide,[5a] and perhalates.[5b] However, with *tert*-butyl hydroperoxide (TBHP) as the primary oxidant, such catalysts, in the presence of nitrogen bases, catalyze two competing reactions, viz., (a) epoxidation (as in Scheme I) and (b) homolytic decomposition of the hydroperoxide.[6,7] The latter reaction, which leads to the formation of 2-methyl-2-propanol and molecular oxygen, also produces allylic oxidation products of substrates such as cyclohexene via a free-radical chain pathway (Scheme II).[8,9] With a view toward minimizing formation of side products, particularly when TBHP is the oxidant, we have undertaken a systematic study on the effect of heterogenization of $Mn[(salen)(H_2O)]PF_6$ (**4**) on kaolinite clay. Our results indicate an improvement in the epoxidation selectivity upon heterogenization of **4**. A comparative account of the performances of the homogeneous catalyst, **4**, and the heterogeneous catalyst, **5**, is presented herein.

Scheme I



LM = metal-porphyrin or metal-salen complex
salen = [*N*,*N'*-ethylenebis(salicylideneaminato)]
YO = single oxygen donor
S = substrate

Scheme II



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