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Superoxide (O_2^-) on the Surface of Heat-Treated Ceria. Intermediates in the Reversible Oxygen to Oxide Transformation

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Powder X-ray diffraction (XRD) and electron spin resonance (ESR) studies were employed for the study of oxygen interaction with nonstoichiometric ceria $CeO_2 \rightarrow CeO_{2-x}$. The crystal structure of CeO_2 is maintained during heat treatment in vacuo from 573 to 1073 K. Oxygen adsorption yields ESR signals for three species believed to all be due to O_2^- adsorbed at different surface sites. Studies of temperature dependence, reactivity, and stability suggested that two side-on-bonded O_2^- species were formed along with an end-on-bonded species probably inserted into a surface oxygen vacancy. This end-on-bonded species behaves as an intermediate in the pathway to re-formation of a lattice oxide dianion.

Introduction

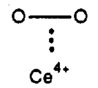
Cerium oxide (CeO_2) is often used in the formulation of oxidation catalysts because of its unique properties. Like many rare earth metal oxides, it is known to readily deviate from a stoichiometric format at elevated temperature and reduced oxygen partial pressure. However, only in the case of ceria is the CeO_2 stoichiometry more energetically favorable ($CeO_{1.5} + {}^1/_4O_2 \rightarrow CeO_{2.0}$, $\Delta G < 0$) than the corresponding sequioxide M_2O_3, and this is due to the relatively favorable electronic configuration of the Ce^{4+} ion. Indeed, CeO_2 has a tendency to remain in its natural fluorite crystal structure even after the loss of considerable amounts of oxygen from its lattice (with the formation of rather high concentrations of oxygen vacancies (V_O)).[1]

Our interest in this system stems from the desire to find model systems for the study of the chemistry of certain types of defect sites. Extensive work with high surface area MgO has indicated that defect sites, perhaps anion/cation vacancies, are important in a variety of surface chemistry processes.[2–7] Unfortunately, determining if vacancies are important is difficult when one is studying MgO or other similar alkaline earth metal oxides, since concentrations of such sites are very low. Thus, we considered the possibility of first trying to understand simple chemical reactions on surfaces where vacancies are known to be prevalent, such as on heat-treated ceria (which has surface chemistry similar in many respects to that of alkaline earth metal oxides). We also hoped to be able to dope ceria with other ions, such as Mg^{2+}, Ca^{2+}, and Y^{3+}.

It seemed as though a likely place to start would be with heat-treated ceria interacting with oxygen. Would it be possible to understand the simple conversion of a vacancy V_O back to an O^{2-} site?

$$V_O + {}^1/_2O_2 \rightarrow O^{2-}{}_{\text{lattice}}$$

There are several studies of O_2^- formation on metal oxides; in particular, the studies of Freed[8] and Howe[9,10] and their co-workers with TiO_2 and SiO_2 should be mentioned. Also there are a number of reports dealing with ceria–O_2 studies. Gideoni and co-workers[11] reported the detection of O_2^-. Che and co-workers[12] also reported O_2^- formation for O_2 interactions on heat-treated ceria supported on silica. Further work by Rojo and co-workers[13] and Fierro[14] confirmed the presence of surface-adsorbed O_2^- on a Ce^{4+} site, which exhibited an ESR spectrum characteristic of an axially symmetric paramagnetic species:



$g_\parallel = 2.033$ $\quad g_\perp = 2.011$

These investigators have generally concluded that only one type of O_2^- species was formed under the conditions of their experiments. However, our results point to additional species. Also, we found no reports concerned with correlating O_2^- surface concentration with V_O concentration. On the other hand, much is known about the defect sites formed, through conductivity studies. These considerations, coupled with a general interest in understanding oxygen surface chemistry,[15,16] prompt us to report our findings.

Experimental Section

All reagents were analytical grade. Pure oxygen was prepared by decomposition of $KMnO_4$. High-purity carbon monoxide was obtained from Matheson Gas Products.

Cerium dioxide was prepared by precipitation of cerium(III) oxalate from water solution (pH = 3) by slow, dropwise addition of dimethyl oxalate to a cerium nitrate solution. The precipitate was dried at 373 K and calcined at 878 K in the air for 4 h. The X-ray diffraction (XRD) powder patterns for samples prepared in this way were very sharp and corresponded exactly to pure CeO_2 with the fluorite crystal structure (face-centered cubic).

About 0.1 g of CeO_2 was placed in an ESR tube and degassed in vacuo at 473 K for 12 h, followed by a slowly increase to the desired temperature, where it was held for another 12 h. The sample was cooled in vacuo and oxygen adsorption carried out at room temperature; about 3 Torr of O_2 was allowed to enter the ESR tube. After 10 min the nonadsorbed O_2 was pumped away until a final vacuum of 1×10^{-3} Torr was attained.

ESR measurements were carried out on an X-band ER 040XR Bruker spectrometer at 9.3 GHz. Diphenylpicrylhydrazyl (DPPH) was used as a standard for *g* value calibrations. X-ray patterns (XRD) were obtained on a Scintag 2000 machine with Cu Kα nickel-filtered radiation.

Results and Discussion

a. Crystal Structure of Ceria Heat-Treated at Different Temperatures. Cerium dioxide samples heat-treated in vacuo at various temperatures (473–1073 K) were examined by XRD for physical changes. Before heat treatment, CeO_2 was bright yellow. After heat treatment, the sample became pale blue and the highest temperatures led to darker blue coloration; such colors are probably indicative of changes in electronic properties with the incorporation

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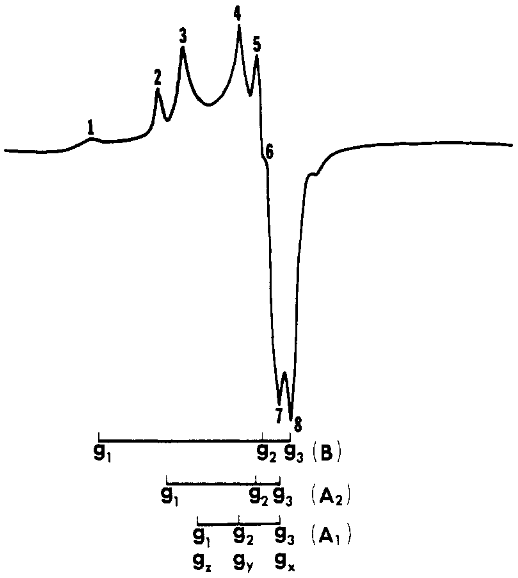

Figure 1. ESR spectrum (77 K) of ceria after heat treatment in vacuo at 673 K, followed by oxygen adsorption at room temperature.

Table I. ESR g Values for O_2^- Species on Ceria

species	g_1	g_2	g_3
A1	2.031	2.018	2.011
A2	2.037	2.014	2.011
B	2.047	2.013	2.0078

of oxygen vacancies (V_O). The XRD patterns did not change with heat treatment temperature, indicating that the CeO_{2-x} retained its fluorite structure at all temperatures employed.

b. Oxygen Adsorption on Heat-Treated Ceria. After 673 K heat treatment in vacuo, no ESR signal was observed for pure CeO_2 at room temperature or at 77 K. (This is in contrast to earlier reports[17-19] of a strong signal at $g = 1.96$.) Upon O_2 adsorption at room temperature, a rather complicated spectrum was recorded (Figure 1). Instead of only one paramagnetic species with $g_\parallel = 2.033$ and $g_\perp = 2.011$ as previously reported,[11-13] we found evidence for several species.

Characterization/identification of these paramagnetic oxygen species will necessitate study of their formation, motion, stability, and reactivity. For clarity of discussion, we will assign tentative structures at this point and consider details later. Briefly, we assign peaks 3, 4, and 7 in Figure 1 to a species labeled A1. Peaks 2, 5, and 7 are assigned to A2, and peaks 1, 6, and 8 to species B. We believe all three species A1, A2, and B are due to superoxide O_2^-, but each is located at a different surface site and with different orientation.

We assign A1 as O_2^- located on surface Ce^{4+} ions with both oxygen nuclei equidistant from the surface (side on). Species A2 is very similar, but the local field is slightly different. Finally, species B we believe is superoxide O_2^- located in surface oxygen vacancies, perhaps inserted into the vacancy (end on). The energy levels and supposed models are depicted in Figure 2 for A1 and B. The g values of all are listed in Table I.

Now we will discuss the properties and behavior of these species.

c. Effect of Different Heat Treatment Temperatures. Earlier studies of heat-treated ceria, using conductivity measurements, X-ray diffraction, and other methods have revealed that the concentration of oxygen vacancies is increased by higher temperatures and lower oxygen partial pressures. Thus, it would be expected that higher concentrations of O_2^- would form upon O_2 adsorption with ceria samples heat-treated at the higher temperatures. (Generally, equilibria are expected on the surface:

$$O_2 \rightleftarrows O_2^- \rightleftarrows O_2^{2-} \rightleftarrows 2O^- \rightleftarrows 2O^{2-}$$

Thus, $[O_2^-]$ may not be proportional to $[V_O]$. In this case, however, we suggest that species B is O_2^- inserted into V_O so the ratio of B to A1 or A2 should increase at higher $[V_O]$.)

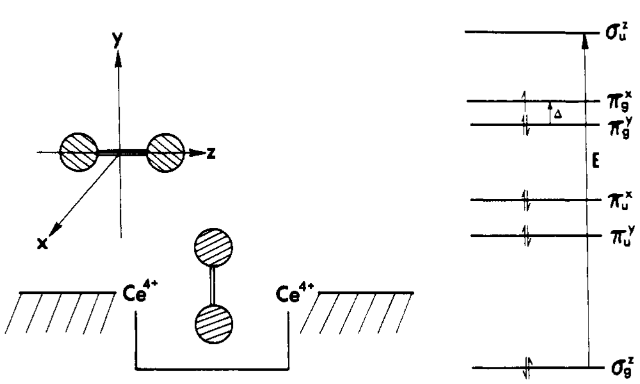

Figure 2. A simple model of oxygen species (O_2^-) on the ceria surface and energy levels for superoxide (O_2^-) species.

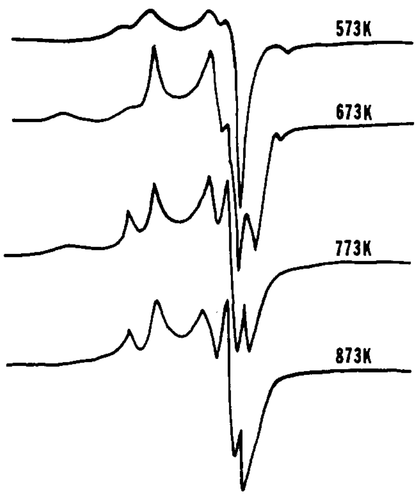

Figure 3. ESR spectra at 77 K of paramagnetic oxygen species (O_2^-) on ceria heat-treated at different temperatures.

Our experimental results are shown in Figure 3. Note that ceria heat-treated in vacuo at 573 K (CeO_2-573) showed no ESR signal for species B after O_2 adsorption. When the heat treatment temperatures were increased, the signal for B gradually increased, as seen by the increase in peak 8 of Figure 1. These results suggest that species B formation is related to V_O surface concentration.

It should be noted, however, that species A1 and A2 also must depend on the availability of oxygen vacancies (V_O). However, it is apparent that species B is more dependent on higher concentrations of V_O.

d. Rotation of Superoxide Species on the Ceria Surface. The orientation of A1, A2, and B on the ceria suface will determine how readily each can rotate or migrate on the surface, and such movement should be temperature dependent.[20,21] As depicted in Figure 4, when sample CeO_2-673 was warmed from 127 to 293 K (after O_2 adsorption), all ESR absorptions broadened gradually, but peak shapes changed in different ways. Peaks due to species B did not change. However, peaks due to A1 did change: g_2 and g_3 overlapped, while g_1 did not change much. These results suggest that A1 gradually became axially symmetric as 293 K was approached; that is, $g_\parallel$ became the same as g_1, while $g_\perp$ became the average of g_2 and g_3. However, the peak for $g_\perp$ overlapped others, and so it was difficult to assign its exact value.

Results obtained when the temperature was lowered from 293 to 127 K and then raised to 226 K show that the peak changes are reversible (Figure 4).

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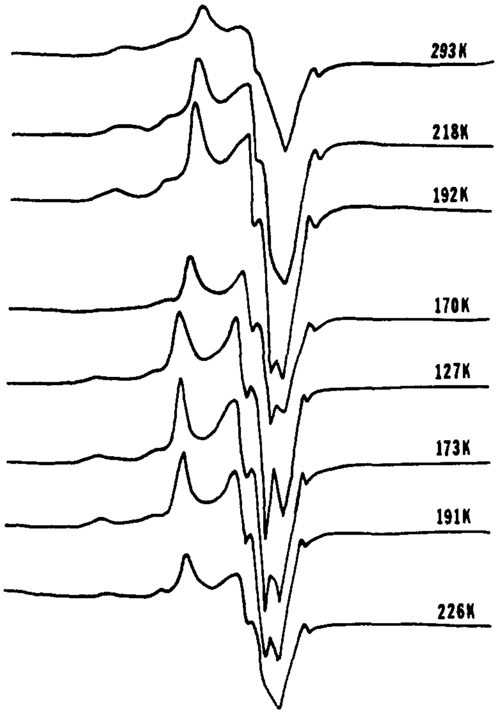

Figure 4. ESR spectra of paramagnetic oxygen species (O_2^-) on ceria at different ESR probe temperatures.

We have assigned A1 as side-on O_2^-, as shown in Figure 2. The y axis is perpendicular to the ceria surface, while the x and z axes are parallel to the surface. Thus, the change in the ESR spectrum could be explained by an increased rate of rotation of species A1 around the z axis. This seems reasonable on the basis of the proposed structure of A1. Likewise, it seems reasonable that B would not so readily rotate on the basis of its proposed structure.

e. Stability of Superoxide Species. It can be conjectured that surface superoxide species could undergo chemical changes by (a) losing an electron to the surface and leaving as a gaseous O_2 molecule and (b) gaining additional electrons and eventually cleaving and take their place as lattice oxide anions (O^{2-}). The ease with which process a would take place should depend on the strength of interaction of O_2^- with the surface. Adsorption of O_2 to form O_2^- and the reverse of this process are usually found to be first-order kinetic processes, dependent on oxygen pressure and surface temperature. On the other hand, further reduction of O_2^- to 2 O^{2-} would be dependent on the availability of electrons and a reaction channel for insertion of oxygen into V_O sites.

To see if we should differentiate species A1, A2, and B with regard to stability, we have employed vacuum treatment and aging studies.

After 5 days of aging at room temperature, peaks due to A1 and A2 were unchanged in shape, although B peaks decreased in intensity when CeO_2-673 was used. Similar results were obtained for a CeO_2-873 sample. It would appear that species B is affected most by aging. These results are supportive of our proposed structural assignment for B.

With regard to the effect of evacuation of oxygen-treated CeO_2-573, CeO_2-673, and CeO_2-873 (10^{-3} Torr for 10 min), no significant changes in spectra were found at room temperature. These results imply that all three species bind strongly to the surface and that lower pressure does not induce back electron transfer and subsequent loss of gaseous O_2.

Heating the CeO_2-673 oxygen-treated sample to 373 K led to the complete loss of all paramagnetic species. This sample was then evacuated for 10 min and cooled to room temperature, followed by readsorption of O_2. Interestingly, peaks of A1 and A2 reappeared, but those for B did not (Figure 5). This reappearance of A1 and A2 indicates that they were reversibly adsorbed/desorbed, depending on temperature. However, for B this is not the case, and so it seems likely that heating of B led to formation of lattice O^{2-} ions. Subsequent readsorption of O_2 did not lead to re-formation of B because the particular sites that form B would now be filled.

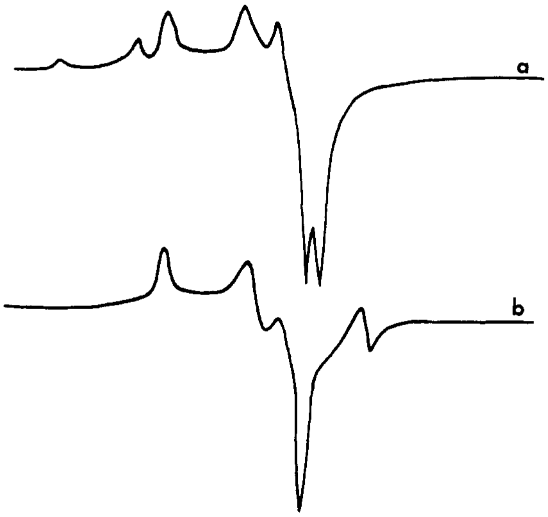

Figure 5. ESR spectra showing that heating at 373 K led to the disappearance of O_2^- and that, after addition of oxygen at room temperature, O_2^- reappeared: (a) before heating; (b) after heating at 373 K and then adding O_2 at room temperature. (Spectra were recorded at 77 K.)

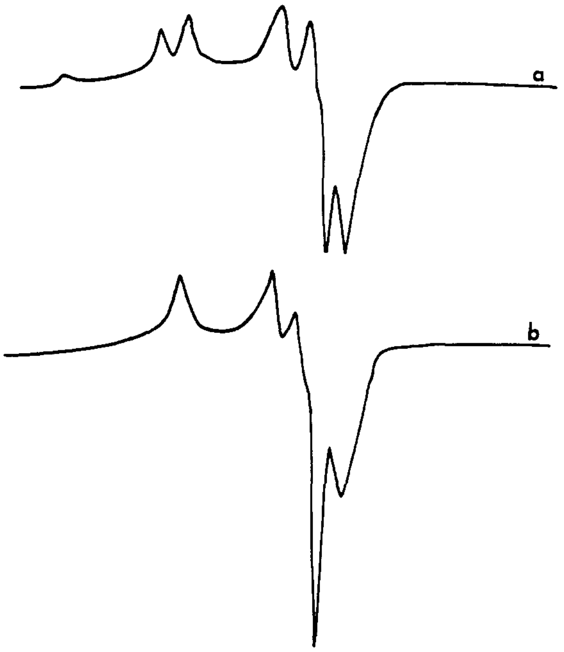

Figure 6. ESR spectra showing that reaction with CO at room temperature led to the disappearance of O_2^- and that, after addition of O_2 at room temperature, O_2^- reappeared: (a) before heating; (b) after reaction with CO and addition of O_2 at room temperature. (Spectra were recorded at 77 K.)

f. Reactivity of Superoxide Species with Carbon Monoxide. The study of the reactivity of surface oxygen species with other molecules can yield information about catalytic oxidation mechanisms.[22,23] We considered that it would be of interest to follow the behavior of species A1, A2, and B when treated with CO. Our procedure was to prepare the A1-, A2-, and B-containing samples, remove excess O_2 by evacuation, treat with 10 Torr of CO at room temperature, age for 10 min, and then evacuate excess CO (down to 10^{-3} Torr). The samples then were again examined by ESR spectroscopy.

The reactivity of A1, A2, and B depended on the ceria heat treatment temperature. For the CeO_2-673 sample at room tem-

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perature, CO addition caused no change. However, for CeO$_2$-873 the A1, A2, and B species all disappeared almost completely upon CO treatment. Interestingly, no selectivity for A1, A2, or B was observed.

After the CeO$_2$-873 sample had been treated with CO, and almost all ESR signals had disappeared, this sample was evacuated at room temperature for 10 min and then treated with O$_2$ again. Species A1, A2, and B reappeared (Figure 6) at lower overall intensities, but the peaks for B were the weakest. This is additional evidence that species B resides at a site significantly different from those of A1 and A2.

It is difficult to understand the dependence of CO reactivity on CeO$_2$ heat treatment temperature. However, it is perhaps not surprising that A1, A2, and B cannot be differentiated by CO reactivity. Although these species can be differentiated by ESR spectroscopy at 77 K, the energy differences between them must be very small compared to the E_a of reaction with CO. Furthermore, the stabilities/lifetimes of the three species depend on each other on the ceria surface. Thus, destruction of B by heating led to a greater instability of A1.

The reappearance of A1, A2, and B when the sample was again treated with O$_2$ is very interesting. It implies that CO does not destroy the active sites. Further investigations are needed in order to better understand this interesting chemistry.

Further Discussion of Structural Assignments

As stated earlier, we believe species A1 and A2 are side-on bonded superoxide species on the surface of nonstoichiometric ceria. On the basis of stability, rotational behavior, and relative abundance on the surface, we believe species B may be superoxide, inserted into an oxygen vacancy, and therefore an intermediate in the re-formation of a lattice O^{2-} by further reduction.

At this point we should discuss why we do not believe other paramagnetic species are responsible for these signals, for example O^- or O_3^-. Although it is difficult to distinguish O^-, O_2^-, and O_3^- by *g* value and line shape (without the use of ^{17}O labeling), it should be possible to differentiate them on the basis of stability and reactivity.

It is known that O_3^- is formed from surface O^- reacting with O$_2$ and that O_3^- usually decomposes back to O^- and gaseous O$_2$ during sample evacuation at room temperature.[24] Our species A1, A2, and B do not behave in this way. It is also known that O^- is extremely reactive, and it has been reported that it reacts with CO at room temperature.[25] Our results show that A1, A2, and B react with similar rates with CO. Actually, they did not react when CeO$_2$-673 was employed, but all reacted when CeO$_2$-873 was employed. This result does not support the idea that we are dealing with O^- species. However, it should be pointed out that we do not understand this striking difference between CeO$_2$-673 and CeO$_2$-873. It seems likely that these differences are due to a higher population of bulk oxygen vacancies in CeO$_2$-873 and their ability to migrate to the surface. However, further work is necessary in order to gain a better understanding.

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Electron Transfer. 112. Reactions of Chromium(IV) with Tin(II) and Cerium(III)[1]

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Aqueous solutions of Cr(IV) may be stabilized through ligation by anions of branched α-hydroxy acids. This atypical oxidation state, prepared at pH 2.5–3.5 in solutions buffered by 2-ethyl-2-hydroxybutanoic acid (HLig) and its anion (Lig$^-$), is readily reduced to bischelated Cr(III) using Sn(II). Kinetic pH and ligand dependencies point to partial conversion of the oxidant to a less reactive deprotonated form and an unreactive "extraligated" form. The pattern of inhibition of the Cr(IV)–Sn(II) reaction by a series of $(NH_3)_5Co^{III}$ cations points to the intervention of a Cr(II) species which reacts with the halogeno-substituted "traps" about 3 times as rapidly as with Cr(IV) in our media. Reactions in the Cr(IV)–Ce(III) system result from superposition of an uncatalyzed bimolecular process and a Ce(III)-catalyzed contribution. The first of these is a disproportionation ($2Cr^{IV} \rightarrow Cr^{III} + Cr^{V}$), whereas the Ce(III)-catalyzed component features competition between oxidative cleavage of the Cr(IV)-bound ligand (to CO$_2$ and 3-pentanone) and Ce(III)-catalyzed disproportionation. Rate dependence on [Ce^{III}] indicates partition of this catalyst between monomeric and dimeric forms, with the latter much less reactive. The observed rate behavior, in conjunction with measured yields of Cr(V), supports a sequence in which the active intermediate, Ce(IV), may undergo a 1e reduction by Cr(IV) or, alternatively, may collaborate with ligand-bound Cr(IV) in an induced electron-transfer process which results in concerted scission of a C–C bond in the ligand and reduction of both quadripositive centers. Differences in the catalytic behavior of Mn(II,III) and Ce(III,IV) are attributed to the recognized specific affinity of Ce(IV) for the alcoholic –OH function.

Solutions of chromium(IV) may be stabilized through ligation by anions of branched α-hydroxy acids such as 2-ethyl-2-hydroxybutanoic acid (I) and may be generated by reductions of

$$(C_2H_5)_2C(OH)COOH$$

I

Cr(VI), in media buffered by these acids, using the 2e donors As(III) and Sb(III).[2] The convenient preparation of this less usual d^2 state has facilitated the investigation of its behavior toward a variety of metal-center reagents, and the kinetic characteristics of the systems Cr(IV)–$Mo_2O_4^{2+}$, Cr(IV)–U(IV), and Cr(IV)–Mn(II) have been found[2,3] to exhibit unexpected facets.

The present contribution deals with the reactions of carboxylato-bound chromium(IV) with tin(II) and cerium(III). The Cr(IV)–Sn(II) system is of interest because it has yielded evidence for the intervention of chromium(II), whereas the lanthanide center has been found to catalyze the reaction of Cr(IV) with the stabilizing ligand. The two systems, viewed together, exemplify contrasting paths by which noncomplementary redox reactions (involving the net 1e oxidant Cr(IV) in conjunction with 2e reductants) may proceed.

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