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Inorganic Chemistry
Viewpoint

# Henry Taube: Inorganic Chemist Extraordinaire

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The numerous innovative contributions of Henry Taube to modern inorganic chemistry are briefly reviewed. Highlights include the determination of solvation numbers and lability, elucidation of substitution mechanisms, discovery and documentation of inner-sphere electron transfer, and discovery of the remarkable coordination chemistry of ruthenium and osmium ammine complexes with unsaturated ligands and mixed-valence complexes and their fundamental relationship to intramolecular electron transfer.

## Introduction

In November 2005, the field of chemistry, especially those of us in inorganic chemistry, lost one of its brightest lights when Henry Taube died just 2 weeks short of his 90th birthday. He was an outstanding scientist and a truly wonderful friend, collaborator, and mentor to his many colleagues and co-workers. He will be sorely missed by those of us who knew him personally and admired him for his intellectual curiosity, his remarkable creativity, and his warm and generous spirit. Reports have appeared documenting the broad details of his scientific career and honors, and some of that information will be repeated here as well. However, our goal is to develop for posterity a retrospective view of his contributions to chemistry.

Henry Taube was born in Neudorf, Saskatchewan, Canada, on November 30, 1915, the son of farmers of German extraction who immigrated to Canada from the Ukraine. His first language at home was Low German, and he occasionally referred to himself as “just a farm boy from Saskatchewan”. He attended the University of Saskatchewan, where he received his BS and MS degrees, and then moved to the University of California at Berkeley, where the School of Chemistry was led by G. N. Lewis and where he earned his Ph.D. in 1940 while working with William Bray. After faculty positions at Cornell University (1941−1946) and the University of Chicago (1946−1962), he moved to Stanford University in 1962. In 1986, he became an emeritus professor, but he continued to carry out active experimental studies at Stanford University until 2001, publishing roughly 90 papers in refereed journals in the period after his “retirement”.

Henry Taube was the recipient of most of the major awards in chemistry, including the 1983 Nobel Prize in Chemistry, the National Medal of Science in 1977, the 1983 Robert A. Welch Award in Chemistry, the 1983 National Academy of Sciences Award in Chemical Sciences, and the 1985 American Chemical Society Priestley Medal. His Nobel citation concludes with the comment “There is no question that Henry Taube has been one of the most creative research workers of our age in the field of coordination chemistry throughout its extent.”

Despite his numerous awards, he retained the perspective of a wise and well-balanced individual. It was characteristic of Henry to devote an award address to describing the contributions of others, and in preparing his Nobel address, he talked frequently to former colleagues in order to credit co-workers accurately, and he cited them generously. When asked about how being awarded the Nobel Prize changed his life, he said, "It was very gratifying and nice to get the recognition. But it didn’t affect my interest or stop me from working. In one sense I felt I had to justify the award."[1]

Henry Taube devoted his career to understanding reactivity and how reactions occur. This was especially true of oxidation−reduction reactions, an area in which he gained preeminence. He was a master experimentalist with a clear understanding of the value of experimental science or, as he said about kinetics, “*The goal for those of us interested in descriptive chemistry is not kinetics as an end in itself, but is rather to understand reactivity ... it (kinetics) being essential to developing the subject of reactivity as a science.*”[2] His experimental work was characterized by creative brilliance, for example, in the use of isotope effects, the determination of solvation numbers, or the detection of intermediates by chemical-trapping experiments. He at-

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(1) Ford, P. C. *Coord. Chem. Rev.* **2005**, *249*, 275−279.
(2) Taube, H. *Chem. Eng. News* **1985**, *63*, 40−45.

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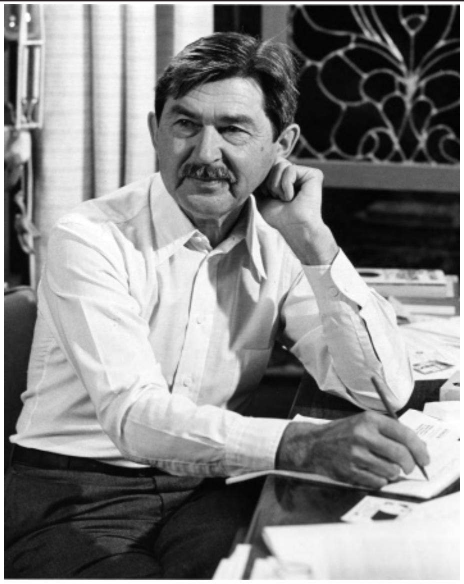


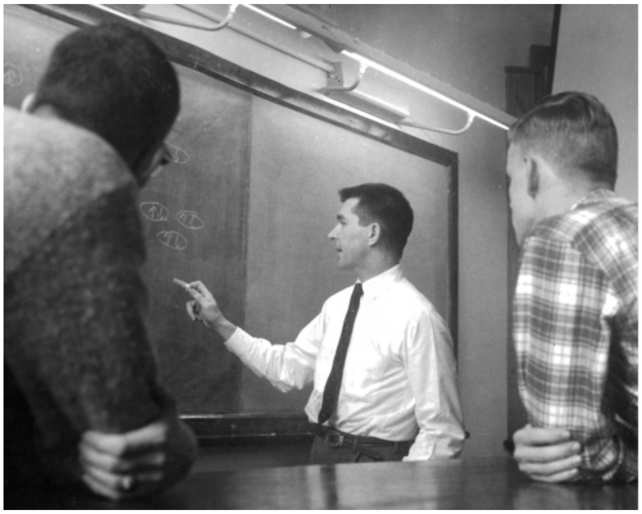
Chuck Painter/Stanford News Service, 1983

Henry Taube was born November 30, 1915, in Neudorf, Saskatchewan, Canada. His parents, of German heritage, had emigrated from Russia. As a boy, Taube spoke Low German and was strongly influenced by the ethical standards of his father "Honest Sam". He studied at the University of Saskatchewan, Saskatoon (BSc, 1935; MSc, 1937), and the University of California at Berkeley (Ph.D., 1940), where he was strongly influenced by Latimer and by his mentor William Bray. His contemporary graduate students include Leo Brewer, R. E. Connick, J. W. Kennedy, E. L. King, T. W. Newton, A. C. Wahl, and W. K. Wilmarth. He took a position as instructor at Cornell University, where he carried out his own experiments on the rates and mechanisms of inorganic redox reactions of nonmetals, for example, ozone and hydrogen peroxide and halide ions. In 1946, he moved to the University of Chicago, where he used a course that he was teaching as a means to learn the fundamentals of transition-metal ions. He was struck by the enormous differences in the rates of substitution of metal ions. During a sabbatical leave spent at the University of California at Berkeley in the late 1940s, he devoted himself to learning about the substitution reactions of transition-metal ions and found a striking correlation with electronic structure, published in 1950 in *Chemical Reviews*. In the early 1950s, he initiated his studies of electron-transfer mechanisms between metal ions in solution, showing first that a chloride attached to Co$^{III}$ in the reactant is transferred to the partner reactant Cr$^{II}$ in the transition state, opening the door to the study of inner-sphere reactions. Taube moved to the University of Stanford in 1962 at about the same time he started the study of Ru complexes. This work subsequently led not only to the advanced understanding of both inner- and outer-sphere redox reactions but also to the discovery of the importance of $\pi$-back-bonding for both Ru$^{II}$ and Os$^{II}$ and their activation (and deactivation) of small molecules ($N_2$, $N_2O$, $H_2$, aromatic hydocarbons) and to the discovery and synthesis of mixed-valence ions. His studies of electron-transfer reactions are his most famous work, for which he won the Nobel Prize for Chemistry in 1983. He received numerous awards and honors, in addition to the Nobel prize, such as the Linus Pauling award in 1981 and the Priestley medal in 1985. Henry Taube died November 16, 2005, just 2 weeks before his 90th birthday. Sources: Taube, H. *Chem. Eng. News* **1985**, *63*, 40−45. Ford, P. C. *Coord. Chem. Rev.* **2005**, *249*, 275−279. Clarke, M. J., private communication to P. C. Ford.

tributed his intuitive but systematic approach to reactivity to his Ph.D. training at the University of California at Berkeley and to his mentor W. C. Bray, and he dedicated his 1985 Priestley address to Bray in Henry's characteristic way of recognizing the contributions of others.[2]

## Research

In his earliest independent work, at Cornell University (1941−1946), Henry Taube focused on oxidation−reduction reactions of the main-group elements with an emphasis on O-transfer reactions involving oxyanions in solution.[3,4] This work included studies on nitrosation by HONO[5,6] and O-atom transfer from halate anions.[7] An additional theme was the development and use of isotopic[3,8] and photochemical (eventually even gas-phase photochemical) methods to explore highly reactive intermediates such as the hydroxyl radical and singlet oxygen, $^1\Delta$ $O_2$. Throughout his career, he maintained a strong interest in the reactions of $O_2$ and other reactive oxygen species,[5,9−16] including the hydroxyl radical,[17] hydrogen peroxide,[18,19] ozone,[9,12,13,15,16,20,21] $CO_3$,[22] and $SO_4^-$.[23] This interest almost certainly derived from his Ph.D. work at the University of California at Berkeley, the topic of which was the reactivity of ozone.[12,13]



## Hydration Numbers, Lability of Metal Complexes, and Substitution Mechanisms

**Hydration of Cations.** Still a relatively junior faculty member in his 30's, but now on the faculty at the University of Chicago in the late 1940s, Henry turned his attention to transition-metal cations in solution. This change in direction

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(15) Le Roy Brough Yeatts, J.; Taube, H. *J. Am. Chem. Soc.* **1949**, *71*, 4100−4105.
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(17) Forchheimer, O. L.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 3705−3706.
(18) Halperin, J.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 380−382.
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was stimulated by teaching an advanced course on transition-metal compounds and deciding to use as a major source a Gmelin volume where the chemistry of cobalt ammines was described rather than using the standard texts then available.[24]

In a remarkable experimental tour de force, he utilized isotopic tracer, spectroscopic, and NMR methods to establish both coordination numbers and labilities of metal complexes.[25] The results of this work transformed coordination chemistry. For the first time, the concept of substitutionally "labile" and "inert" was introduced based on practical, experimental distinctions. *Labile* referred to metal ions for which substitution was complete on the time scale of mixing, while *inert* was used to describe metal ions with substitution rates slow enough to follow by conventional mixing techniques using color changes, for example. This distinction between labile and inert, initially derived for coordination compounds, has since permeated all of science from biology to materials science. It also germinated his seminal studies on the mechanism of electron transfer between metal complexes in solution (see below).

In his book *Electron-Transfer Reactions of Complex Ions in Solution*, Taube begins with an exposition of cation hydration followed by coordination numbers and lability and traces the importance of these topics in understanding electron transfer.[26] The lability of a hydrated metal ion determines the techniques that are applicable for the determination of its coordination number. Previously, hydration numbers had been inferred by comparing ligand-field spectra in solution to those of structurally characterized solids; for example, in water, $Co^{2+}$ is pink and therefore was assumed to be six-coordinate, in analogy to similarly colored solids that are six-coordinate, rather than four-coordinate, which are blue in their solids.

In 1950, Henry Taube and John P. Hunt reported a direct solution measurement of the coordination number and rate of ligand exchange with solvent water ($t_{1/2} \sim 40$ h) of the inert $Cr(H_2O)_6^{3+}$ ion, using a Taube-invented "hold-back"[27] technique.[28,29] In this experiment, an aliquot of $^{18}O$-enriched water was added to an aqueous, acidic solution containing $Cr(H_2O)_6^{3+}$. Samples of the solvent were removed at various times and their declining $^{18}O$ content determined by mass spectrometry to determine both the kinetics of water exchange and the coordination number.[30] In these experiments, $^{18}O$-labeled water was equilibrated with $CO_2$ and the $^{18}OC^{16}O/^{16}OC^{16}O$ ratio determined by mass spectrometry. Alan Sargeson has pointed out that Taube was drawn to isotopic measurements while at the University of Chicago by both the isotopic chemistry then under development at the University of Chicago and nearby Argonne National Laboratory and the utilization of Nier mass spectrometers at the University of Chicago.[31]

In 1952, Henry Taube published a justifiably famous review on the substitution rates of metal ions.[32] Although stimulated by the course he taught at the University of Chicago, the origin of the review was in his rigorous study of the primary literature on ligand substitution rates during a sabbatical leave at the University of California at Berkeley as a Guggenheim fellow. The product of this effort was more than a review because it accounted for lability based on the electronic structures of metal ions. In its initial formulation, his arguments utilized valence-bond terms such as "inner orbital" and "outer orbital" that were later recast in crystal-field terms by Basolo and Pearson.[33]

Taube linked lability to cation charge, radius, and electronic structure. For six-coordinate complexes, substitution tends to be slow when only the three $d\pi$ orbitals, the nonbonding $t_{2g}$ orbitals in octahedral complexes, are occupied.[24] With these arguments, he was able to rationalize diverse rate constants for water exchange, which for $M(H_2O)_6^{3+}$ complexes varied widely from $V(H_2O)_6^{3+}$ $(t_{2g})^2$ at $1 \times 10^3$ s$^{-1}$ to $Cr(H_2O)_6^{3+}$ $(t_{2g})^3$ at $5 \times 10^{-6}$ s$^{-1}$ and for $M(H_2O)_6^{2+}$ varied from $V(H_2O)_6^{2+}$ $(t_{2g})^3$ at $8.7 \times 10^1$ s$^{-1}$ to $Cr(H_2O)_6^{2+}$ $(t_{2g})^3(e_g)^1$ at $1.2 \times 10^8$ s$^{-1}$.[34]

The following is an excerpt:

> *"The factor of great importance in determining the behavior of complex ions is the rate at which substitution reactions for them take place. It is, in fact, of greater importance for many of the observations that are made than is the factor of stability.... While it may seem superfluous to stress that there is no necessary connection between slow rate and stability, considerable confusion in understanding the behavior of complex ions has resulted because of the failure to distinguish between the rate and the equilibrium aspects."*[32]

Taube utilized another oxygen isotope, spin $^5/_2$ $^{17}O$, to great advantage in the study of aqua cations. For paramagnetic metal ions, the temperature dependence of the line width allowed the evaluation of the rates of water exchange. (See refs 35 and 36.) Typical of his experimental ingenuity, he utilized paramagnetic shifts and $^{17}O$ NMR to determine hydration numbers. Paramagnetic ions broaden the $^{17}O$ NMR resonance in $H_2{}^{17}O$. The addition of labile paramagnetic ions to solutions containing a second, inert ion broadened the solvent resonance, allowing direct observation and integration of coordinated water for the second ion. Henry was personally involved in determining exchange rates for $Cr(H_2O)_6^{3+}$ [28,29] and $V(H_2O)_6^{2+}$,[37] among others.

The mechanistic details of how substitution reactions occur were also addressed by Taube and his group. This included

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(25) Taube, H. *J. Chem. Soc., Dalton Trans.* **1991**, 547−553.

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(30) Indeed the development of the entire electron-transfer field benefited from the pre- and post-World War II production of isotopes. The first self-exchange between $Pb^{II}$ and $Pb^{IV}$ was reported in 1920. See: Seaborg, G. T. Artificial Radioactivity. *Chem. Rev.* **1940**, *27*, 199−285. Both radioactive and nonradioactive isotopes proved useful in mechanistic studies.

(31) Sargeson, A. Private communication, 2006.

(32) Taube, H. *Chem. Rev.* **1952**, *50*, 69−126.

(33) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; John Wiley and Sons: New York, 1958.

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(35) Friedman, H. L. *Chem. Scr.* **1985**, *25*, 42−48.

(36) Helm, L.; Nicolle, G. M.; Merbach, A. E. *Advances in Inorganic Chemistry—Including Bioinorganic Studies*; Elsevier: New York, 2005; Vol. 57, pp 327−379.

(37) Olson, M. V.; Kanazawa, Y.; Taube, H. *J. Chem. Phys.* **1969**, *51*, 289−296.

recognition of the importance of preassociation prior to substitution[38,39] and a series of intellectually impressive experiments designed to distinguish between $S_N1$ (dissociative) and $S_N2$ (associative) mechanisms in hydrolysis and base-catalyzed hydrolysis reactions.[40] In these experiments, induced substitution was used to create good leaving groups and lower-coordinate intermediates whose subsequent reactivities were probed by competitive capture by added nucleophiles and by determination of their product stereochemistries.[40−45]

## Electron-Transfer Reactions of Transition-Metal Complexes

Henry Taube's interest in electron transfer can be traced to his early studies on redox reactions involving halogens[46−48] including transition-metal ions acting as catalysts.[49−51] He had also encountered electron transfer and its influence on substitution at $Au^{I}$ [52] and in the catalysis of the $Pt^{IV}-Pt^{II}$ exchange.[53] However, his lasting contributions to this area, and the basis for his later Nobel prize, came when his interest turned to electron transfer between metal complexes. This shift in emphasis was triggered by his new-found understanding of metal ion lability.

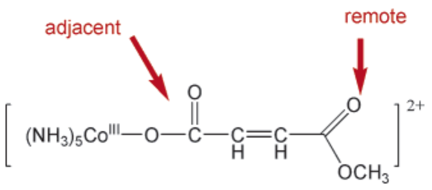
**Inner-Sphere Mechanism.** With an understanding of substitution and lability, Taube had established a basis for studying electron-transfer mechanisms. An initial elementary experiment in this area stands out as one of the most revealing ever performed in a chemistry laboratory. In this experiment, $Cr^{2+}_{aq}$ was mixed with $(NH_3)_5CoCl^{2+}$. Initially, this was a test tube experiment with results deduced from the color change that occurred from the sky blue of $Cr^{2+}_{aq}$ and the purple of $(NH_3)_5CoCl^{2+}$ to the deep green of $(H_2O)_5CrCl^{2+}$. This led him to conclude that electron transfer from $Cr^{2+}_{aq}$ to $Co^{III}$ was accompanied by transfer of the $Cl^-$ ligand and led to the definition of inner-sphere electron transfer. In his words,[54]

> *"An important problem in the field of mechanisms of "electron transfer" reactions is concerned with the changes taking place in the coordination spheres of the oxidant and the reductant on electron transfer.... Thus it is not known whether electron transfer takes place by an electron jump through several layers of solvent, or whether it accompanies the transfer of a group such as OH from oxidant to reductant; or H from reductant to oxidant.... The principal reason for the lack of detailed understanding is that systems are generally very labile. ... One method of attack on these problems is to ... exploit the ions that are less labile with respect to substitution under ordinary conditions. ... We have followed this line of attack, choosing the reductant $Cr^{2+} \rightarrow Cr(III)$. This system has the virtue that any group found in the coordination sphere of Cr(III) when it is formed from $Cr^{2+}$ must have been present in the activated complex. Substitution reactions of Cr(III) are sufficiently slow so that entry of groups after completion of the oxidation can be ruled out...."*

The appearance of $CrCl^{2+}$ provided direct evidence for an inner-sphere mechanism because cobalt(III) ammine and chromium(III) complexes are substitutionally inert. This meant that the transferred chloride initially bound to $Co^{III}$ was also bound to labile $Cr^{2+}$ when electron transfer occurred. The observed color change allowed Taube to invoke a ligand-bridged activated complex such as $[(NH_3)_5Co^{III}-Cl-Cr^{II}]^{4+}$. In contrast, when the coordination sphere of the $Co^{III}$ center does not contain a ligand with the appropriate properties to serve as a bridge between two metal centers, electron transfer must occur by another (outer-sphere) mechanism. For example, not only is the $Cr^{2+}$ reduction of $Co(NH_3)_6{}^{3+}$ much slower than the analogous reaction with the chloro complex, but ligand transfer to the $Cr^{III}$ product is not found in this case.

As noted in his Nobel address,[24] *"the bulk of the work in these two papers* (refs 54 and 55) *was carried out with my own hands."*

**Adjacent or Remote Attack?** At the University of Chicago, Taube next became interested in organic ligands as bridging groups and used carboxylatocobalt(III) complexes to explore the impact of the ligand structure on inner-sphere electron-transfer rates and mechanisms. One aspect of great interest was the site of reductant attack.[56,57] In carboxylate ligands with more than one potential binding site, where does the $Cr^{2+}$ attack? With an unsaturated ligand such as fumarate, shown below, could attack occur at the remote carbonyl with the C−C double bond providing a conduction pathway?[58]



The results of initial studies with coordinated maleic and fumaric half-esters[59−64] were consistent with "remote attack", but, unfortunately, these results were not reproducible and were later corrected after Taube had moved to Stanford University.[65,66] However, it should be noted that remote attack

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(38) Taube, H.; Posey, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 1463−1467.
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(41) Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* **1957**, *79*, 255−262.
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(44) Loeliger, D. A.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1376−1380.
(45) Dolbear, G. E.; Taube, H. *Inorg. Chem.* **1967**, *6*, 60−64.
(46) Taube, H. *J. Am. Chem. Soc.* **1942**, *64*, 161−165.
(47) Taube, H. *J. Am. Chem. Soc.* **1943**, *65*, 1876−1882.
(48) Hochhauser, I. L.; Taube, H. *J. Am. Chem. Soc.* **1947**, *69*, 1582−1589.
(49) Taube, H. *J. Am. Chem. Soc.* **1947**, *69*, 1418−1428.
(50) Taube, H. *J. Am. Chem. Soc.* **1948**, *70*, 1216−1220.
(51) Taube, H. *J. Am. Chem. Soc.* **1948**, *70*, 3928−3935.
(52) Rich, R. L.; Taube, H. *J. Phys. Chem.* **1954**, *58*, 6−11.
(53) Rich, R. L.; Taube, H. *J. Am. Chem. Soc.* **1954**, *76*, 2608−2611.
(54) Taube, H.; Myers, H.; Rich, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 4118−4119.
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(57) Taube, H. *Bunsen-Ges. Phys. Chem.* **1972**, *76*, 964.
(58) Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321−329.
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(62) Fraser, R. T. M.; Taube, H. *J. Am. Chem. Soc.* **1960**, *82*, 4152−4153.
(63) Fraser, R. T. M.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 2239−2242.
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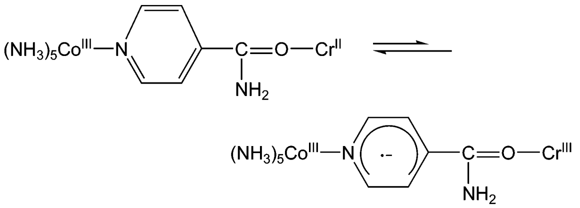
(66) Olson, M. V.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2072−2081.

by the reducing agent $Cr^{2+}$ through a $\pi$-unsaturated organic bridging ligand was demonstrated by Nordmeyer and Taube in 1966 by using the pentaamminecobalt(III) complex of isonicotinamide in an experiment that is described in more detail below.[67]

**Chemical Mechanism.** The $Cr^{2+}_{aq}-Co^{III}$ pairing was used to great effect to demonstrate inner-sphere mechanisms. A key was isolation and characterization of the initial (metastable) $Cr^{III}$ product. For certain pyridyl ligands, such as isonicotinamide, remote attack occurs, and there is strong evidence for a "chemical mechanism" (currently called a "hopping mechanism") in which an electron is transferred to the ligand in an unfavorable preequilibrium with rate-determining capture by the pyridyl-attached oxidant, $Co^{III}$ or $Cr^{III}$, e.g.,[57,58,68]



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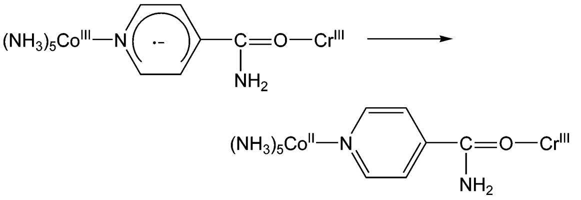


(2)

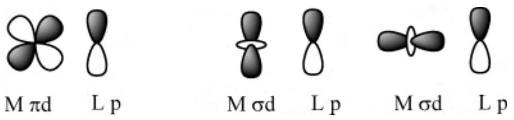
The intervention of ligand-radical intermediates was also demonstrated by one-electron oxidation of a coordinated ligand, with one-electron oxidants such as $Ce^{IV}$ leading to reduction at $Co^{III}$, for example, in the pyridinemethanol complex $[(NH_3)_5Co\text{-}p\text{-}NC_5H_4CH_2OH]^{2+}$.[69]

**New Oxidant, $Ru^{III}$.** When $d\pi^6$ $Co^{III}$ was replaced by $d\pi^5$ $Ru^{III}$, product studies revealed an inner-sphere mechanism, but the reaction was far too rapid to invoke the two-step mechanism in eqs 1 and 2.[70] Gaunder and Taube attributed the reactivity enhancement to extensive mixing of the $d\pi$ and bridging ligand $\pi$ systems although, in retrospect, another contributing factor is that the $Ru^{III}$ center in the bridged complex is a much stronger oxidant than analogous $Co^{III}$ or $Cr^{III}$ centers.

## Spectroscopy and Reactivity of Ruthenium and Osmium Ammines

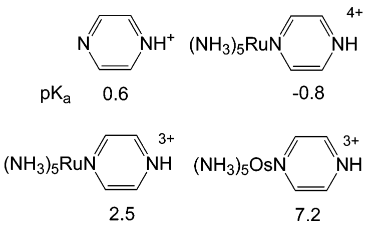
**$\pi$-Back-Bonding and Metal-to-Ligand Charge-Transfer (MLCT) Absorption.** As noted above, Taube chose to investigate the electron-transfer reactions of $(NH_3)_5RuL^{3+}$ complexes because these provided model oxidants for comparison with the extensively studied $(NH_3)_5CoL^{3+}$ analogues but with an acceptor orbital ($t_{2g}$) having $\pi$ symmetry rather than the $\sigma$-symmetry acceptor orbital ($e_g$) characterizing the $Co^{III}$ systems. Another difference is that the inner-sphere reorganization energy is much smaller for $Ru^{III}-Ru^{II}$ than for $Co^{III}-Co^{II}$. This is because the change in the electronic configuration at Co, from $d\pi^6$ to $d\pi^5 d\sigma^{*2}$, results in a significant increase in metal−ligand bond distances upon reduction. The increase in the electron-transfer barrier is significant, with outer-sphere reduction of $Ru(NH_3)_6^{3+}$ by $Cr^{2+}$ being $10^6$ times faster than that of $Co(NH_3)_6^{3+}$[71,72] and the self-exchange rate of the hexaammineruthenium couple, $8 \times 10^2\ M^{-1}\ s^{-1}$ being 8 orders of magnitude greater than that for the analogous cobalt ammines.[73]

Another property of great interest became apparent for the Ru complexes. Although the colors of carboxylatoruthenium(III) complexes are unremarkable,[72] the $Ru^{II}$ forms containing aromatic N-heterocyclic ligands, such as pyridine or pyrazine, are highly colored. The absorption bands responsible for these colors proved to be very sensitive to parameters such as solvent and ligand substituents, consistent with their assignment as MLCT absorptions.[74] The low energies and high intensities of MLCT absorption bands implicate strong mixing of metal-based $d\pi$ and ligand-based $\pi^*$ levels.[75] The symmetries of the $d\pi$ and $d\sigma^*$ metal donor orbitals relative to the ligand $\pi^*$ acceptor orbitals are illustrated as follows:



In subsequent work, the photochemistry of the $Ru^{II}$ complexes was investigated in detail and the sensitivities of the MLCT energies to the ligand substituents and media were used to tune the excited-state reactivities.[76−78]

The $d\pi^6-\pi^*$ interactions are even greater for analogous $Os^{II}$ complexes.[79,80] This is because of the enhanced $5d\pi$ orbital extension compared to $4d\pi$ and a closer energetic match of the donor and acceptor orbitals. Ground-state $d\pi-\pi^*$ mixing is also important and responsible, for example, for the extraordinary stability of the $M(NH_3)_5(N_2)^{2+}$ dinitrogen complexes and, as shown by the data below, enhanced basicity of pyrazine when it is bonded to $Ru^{II}$ or (and) $Os^{II}$.[74,79,81] In addition, there is a significant relationship between the spectral properties, redox potentials, and reactivity in these complexes.



The intricate interplay between the metal and ligand identified in these data foreshadowed an extensive reactivity of coordinated ligands, an area later developed quite spec-

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**Table 1.** Equilibrium and Reduction Potential Data

| | M = Ru | | M = Os |
|---|---|---|---|
| L | $E^0$, V vs SHE | $K_L$,[a] $M^{-1}$ | $E^0$, V vs SHE |
| $NH_3$ | +0.05[b] | $3.5 \times 10^{4}$ [90] | −1.02[c] |
| $N_2$ | | $3.3 \times 10^{4}$ [91] | |
| $M(NH_3)_5N_2^{2+}$ | 1.2, 0.73[92] | $7.3 \times 10^{3}$ [91] | +1.4, −0.16[92] |
| $N_2O$ | | 7.0[93] | |
| pyridine | +0.298[b] | $2.4 \times 10^{7}$ [86] | −0.395[80] |
| isonicotinamide | +0.375[b] | | −0.24[80] |
| pyrazine | +0.49[b] | | −0.09[80] |
| $M(NH_3)_5(pyrazine)^{2+}$ | +0.77, +0.38[94] | | +0.32, −0.44[94] |
| $H_2O$ | 0.10[95] | 1 | −0.73[88] |
| $H_2S$ | −0.12 | $1.5 \times 10^{3}$ [95] | |
| $HS^-$ | −0.29 | $1.5 \times 10^{6}$ | |

[a] The standard state for gases is 1 M, not 1 atm. [b] Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107−1110. [c] Gulens, J.; Page, J. A. *J. Electroanal. Chem.* **1976**, *67*, 215−230.

tacularly by Harman and Taube, among others. (In contrast, for the case of $N_2$ binding, where Armor's equilibrium studies established the sobering fact that it is easier thermodynamically to reduce free $N_2$ than $N_2$ bound to $Ru^{II}$.) This reactivity was an offshoot of Taube's interest in the organometallic-like chemistry of complexes of "innocent" amine ligands, which are $\sigma$ donors and not $\pi$ acceptors. Investigation of such complexes would provide insights that link conventional coordination chemistry and organometallic chemistry.[82,83]

The $Ru^{II}$ complexes $(NH_3)_5RuL^{2+}$ containing $\pi$-acceptor ligands are synthesized from the moderately labile[84] complex $(NH_3)_5RuOH_2^{2+}$ with second-order rate constants[74,85,86] approaching $10^{-1}\ M^{-1}\ s^{-1}$ in the presence of excess L. The once-oxidized $(NH_3)_5RuL^{3+}$ forms are inert. $(NH_3)_5OsOH_2^{2+}$ is too reducing for synthesis in water to be successful.[87] The best synthetic route found was the use of the triflate complex, $[(NH_3)_5Os(CF_3SO_3)](CF_3SO_3)_2$, in organic solvents.[88,89] Data for the equilibrium

$$L + (NH_3)_5MOH_2^{\ 2+} = (NH_3)_5ML^{2+} + H_2O \qquad K_L \tag{3}$$

are given in Table 1. Only reduction potential data are available for the Os complexes.

Interesting observations appear in the data including the ca. 1000-fold preference of $Ru^{II}$ for pyridine (py) over ammonia. For $Ni^{II}$, the preference is ca. 10.[86] Similarly, the influence of back-bonding ligands such as pyridine or pyrazine in increasing the $M^{III}-M^{II}$ reduction potentials is notable. With S ligands, back-bonding to vacant S d orbitals plays an important role in stabilizing $Ru^{II}-S$ bonds in complexes of hydrogen sulfide, thioether, dimethyl sulfoxide (DMSO), and even the cationic trimethylsulfonium ligands.[95−97]

**Reactions of Coordinated Ligands.** In 1967, Harrison and Taube reported[98] the spontaneous binding of $N_2$ to aquopentaammineruthenium(II) to give the $(NH_3)_5Ru(N_2)^{2+}$ complex, which was first reported by Allen and Senoff,[99] who discovered this complex as a product in the reaction between $RuCl_3{\cdot}xH_2O$ and hydrazine in water. There was immediate interest in this work in laboratories around the world because of the possibility of finding practical routes for N fixation.[100,101] With this impetus, work in the Taube laboratory was focused on $N_2$ reduction, which led to studies of ruthenium[102,103] and osmium[104,105] ammine complexes with $N_2$ and other small molecules. Armor and Taube characterized the kinetics and thermodynamics of the formation of the $N_2$ monomer and dimer,[91] as well as a highly unusual complex of nitrous oxide.[106,107] They also discovered the rapid reaction of nitric oxide with $Ru(NH_3)_6^{3+}$ to give $Ru(NH_3)_5NO^{3+}$.[108]

One strategy applied at that time was to try to induce internal disproportionation of a $\mu$-$N_2$ bridge, i.e., $Ru^{III}N{\equiv}NRu^{III} \rightarrow 2Ru^{VI}N^{3-}$.[109] Both ruthenium aqua[109] and osmium ammine[92] complexes failed to produce the desired result. However, in 1991, Ware and Taube[110] reported evidence for the reverse process, with osmium nitride complexes yielding $N_2$-bridged $Os_2$ dimers in the presence of pyridine. In this work, it was also shown that the nitrido complex could be reduced to an osmium(III) ammine.[111] The appearance of $N_2$-bridged dimers was also demonstrated when $(NH_3)_5OsCO^{2+}$ was oxidized by $Ce^{IV}$.[112]

**Organometallic Chemistry of Osmium(II) Ammines.** Harman and Taube further demonstrated that osmium(II) ammine complexes had considerable differences compared to their $Ru^{II}$ homologues. For example, reaction

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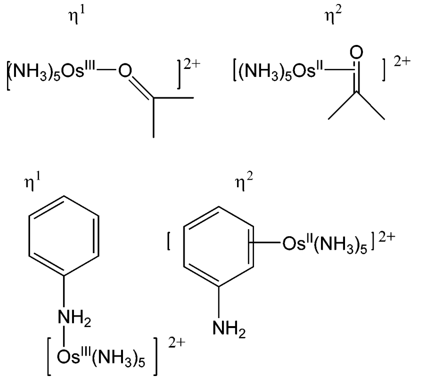
with benzene gives the stable organometallic compound $(NH_3)_5Os(benzene)^{2+}$, which persists when dissolved in water.[113] While $\eta^6$ piano stool complexes of $Ru^{II}$ with benzene, such as $Ru(benzene)(H_2O)_3^{2+}$, were known,[82] there was no precedent for the $\eta^2$-bound aromatics found for osmium(II) ammines[83] (except as proposed intermediates in the flash photolysis of ruthenium ammine complexes), and such species proved to be of interest in the context of C−H activation.[114] The electrochemistry of these organometallic complexes abounds with redox-state-dependent linkage isomerization, as illustrated in the following for acetone[115,116] and aniline:[117]



Remarkably, these reactions are intramolecular in nature, occurring without hydrolysis, pointing to intermediate bonding states of considerable stability. These studies also revealed an affinity of $d\pi^5$ $Os^{III}$ toward $N_2$, benzene, etc. There is also evidence for the ability of $Os^{III}$ to back-bond in the MLCT spectra of $Os^{III}$ complexes.[80] Related linkage isomerizations are found for ruthenium ammine complexes but with ligands such as glycine,[118] imidazoles,[119] urea,[120] DMSO,[121] xanthine,[122] and $N_2$.[123] Intramolecular migration of $Ru^{II}$ from amide to pyridyl binding sites following hydrolysis and reduction of the nitrile complex is related to the $Os^{II}$ migrations.[124]

The $\eta^2$ coordination to $(NH_3)_5Os^{II}$ appears to interrupt the aromaticity of a benzene or other aromatic ligand. As a consequence, a second $Os^{II}$ or even a $Ru^{II}$ can be subsequently added. Furthermore, the loss of aromaticity makes the ring susceptible to attack by both electrophiles and nucleophiles and susceptible to ring hydrogenation with either heterogeneous or homogeneous catalysts under conditions at which the original aromatic molecule is unreactive.[83] The activation of organic ligands by osmium ammines and related metal complexes continues to be studied.[125]

**Osmium Ammine Complexes of $H_2$ and Hydride.** Malin and Taube reported the complex $Os(en)_2(H)_2^{2+}$, which was described as a dihydride and assigned a cis configuration.[126] Prompted by Kubas' discoveries of $\eta^2$-$H_2$ complexes,[127,128] in 1991 Li and Taube prepared the analogous tetraammine complex and discovered it to be $Os(NH_3)_4(\eta^2\text{-}H_2)^{2+}$, a 16-electron $H_2$ complex.[129] In 1994, the related $H_2$ complex $[Os(en)_2(CH_3CO_2)(\eta^2\text{-}H_2)]PF_6$ was reported to contain $\eta^2$-$H_2$ with an H−H distance of 1.34 Å, bound trans to the acetate.[130] $\pi$-Acid ligands were found to draw the H atoms together as shown by the high value of the $J_{HD}$ coupling constant. An isonitrile ligand induces $H_2$ loss from the Os complex. Weak nucleophiles produce the opposite effect and could, in principle, form a dihydride, but it would have to be seven-coordinate, for which there are examples in the polypyridyl chemistry of Os.

It is notable that the large majority of Henry Taube's papers on the remarkable chemistry of osmium ammines were published after his "retirement" in 1986.

## Mixed-Valence Ions and Intramolecular Electron Transfer

**Soluble Mixed-Valence Ions.** The enhanced basicity of pyrazine in $(NH_3)_5Rupz^{2+}$ suggested the use of pz as a bridge between two centers, and Taube and Ford prepared the pyrazine-bridged diruthenium(II) dimer at Stanford University in 1966.[24] In 1967, seminal articles also appeared by Robin and Day[131] and by Hush[132,133] reviewing and defining the properties of mixed-valence materials. The Robin and Day classification scheme for bridged complexes defines class I as those displaying properties that are the sum of the isolated centers. At the other extreme, class III complexes display electronic delocalization and properties significantly different from those of the constituents.

From the standpoint of electron-transfer models, class II systems of ligand-bridged mixed-valence complexes, e.g., $M^{II}{-}B{-}M^{III}$ (B is a bridging group) in which electronic coupling is moderate, are the most interesting. In these complexes, the isolated properties of the components are preserved, although perturbed slightly, and a new optical transition (eq 4) appears that is directly related to thermally activated electron transfer. In this case, the asterisk denotes

$$M^{II}{-}B{-}M^{III} \xrightarrow{h\nu = E_{op}} (M^{III}{-}B{-}M^{II})^* \qquad (4)$$

the formation of an initial state of $M^{II}{-}B{-}M^{III}$ in which the coupled solvent and vibrational modes are in excited levels.

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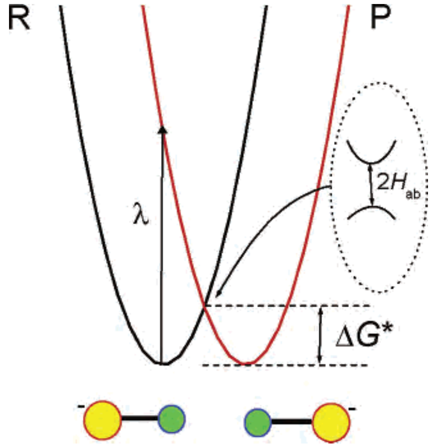


Figure 1.

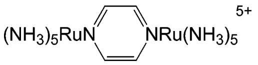
For the example shown in Figure 1, the coordination spheres of the two metal centers are identical with $\Delta G^0 = 0$ for electron transfer. Light absorption occurs with $h\nu = \lambda$, the classical reorganization energy for the electron transfer.[133] Because of the parabolic nature of reactant (R) and product (P) surfaces, the reorganization energy is related to the free energy of activation for electron transfer by $\lambda = 4\Delta G^*$, as shown initially by Hush. The reactant and product surfaces are split at their intersection by the quantity $2H_{ab}$, where $H_{ab}$ is the electronic coupling element for electron transfer (blown up to the right of the figure). The intervalence transfer or IT spectrum of a class II mixed-valence species can therefore provide information about the kinetic barrier to thermal electron transfer. The absorption maximum and bandwidth at half-height give $\lambda$, and the integrated intensity gives the extent of electronic coupling, $H_{ab}$.[133]

The relationship between $\lambda$ and $\Delta G^*$ arises because, from the Franck−Condon principle, electron motion occurs on a time scale at which both the metal−ligand and surrounding solvent nuclear positions are frozen. Light absorption results initially in a "Franck−Condon" state in which the electron is transferred but the nuclei remained fixed, no longer in their equilibrium positions.

*"In turning now to the past, the outstanding feature of the history of the early advances in understanding electron transfer reactions appears to me to be the central role which the Franck−Condon restriction played in its development. Principles are the girders on which the structures of science are erected. The power of the Franck−Condon Principle in crystallizing the thinking about the rates and mechanisms of electron transfer reactions in chemical systems and, almost from the onset, in providing direction to the experimental work, constitutes a textbook illustration of the statement."*[134]

Many examples of IT absorption have been identified and described in the literature.[131,132] In the classic example of Prussian blue, a ferricyanide/ferrocyanide solid, the blue color arises from IT between chemically inequivalent iron centers, $Fe^{II}$ surrounded by cyanide C atoms and $Fe^{III}$ surrounded by cyanide N atoms, with $B = NC^-$.[135] In this case, the coordination asymmetry induces a net free-energy change, $\Delta G^0$, between the initial and final states and it contributes to the energy of the absorption maximum with $h\nu_{max} = \lambda + \Delta G^0$.

In 1969, IT absorption in the mixed-valence, pyrazine-bridged complex



(later known as the Creutz−Taube ion) was found in the near-IR at 1570 nm.[136] Describing the properties of this system has preoccupied the study of mixed-valence materials since, both experimentally and theoretically. It appears to be poised between classes II and III in the Robin−Day scheme, with complications arising from multiple IT transitions and the time scales of coupled vibrations and the solvent.[137,138] By contrast, the 4,4′-bipyridine-bridged dimer is clearly in class II.[139]

Shortly after the Creutz−Taube ion was described, an IT band was also reported in a linked ferrocene/ferrocenium complex.[140] The synthesis and IT absorption band properties of mixed-valence species have proven to be extremely important to our understanding of electron transfer because fundamental information concerning barriers and electronic coupling can be obtained from simple spectral measurements. An example is the solvent and distance dependences of charge transfer in the series $[Ru(bpy)_2Cl]_2(B)^{3+}$ with B = pyrazine, 4,4′-bpy, etc.[141] The field of mixed-valence chemistry has grown enormously since the first reports from Taube's laboratory,[142−148] and a number of recent reviews or reports are available for inorganic[141,149] and organic systems.[150−152]

**Intramolecular Electron Transfer.** For nonadiabatic electron transfer, the electron-transfer rate constant ($k_{et}$) can be expressed as the product of a nuclear frequency ($\nu_n$) and the electronic ($\kappa_{el}$) and nuclear ($\kappa_n$) factors:[153]

$$k_{et} = \kappa_{el}\nu_n\kappa_n = \frac{k_BT}{h}\exp\left(-\frac{\Delta H^*}{RT}\right)\exp\left(\frac{\Delta S^*}{R}\right) \qquad (5)$$

Intramolecular electron-transfer rates have been measured in selected bridged systems. In work initiated by Isied[154] and

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continued by others in Henry's laboratory,[155−157] electron transfer in the complexes $(NH_3)_5Co^{III}-B-Ru^{II}(NH_3)_5{}^{5+}$ was initiated by outer-sphere reduction of the corresponding $Co^{III}-B-Ru^{III}$ complex with hexammineruthenium(II). Rate constants and activation parameters for subsequent intramolecular $Ru^{II} \rightarrow Co^{III}$ electron transfer have been considered by comparison with IT for the analogous mixed-valence diruthenium complexes $(NH_3)_5Ru^{III}-B-Ru^{II}(NH_3)_5{}^{5+}$.[158] Extensive studies of other inner-sphere systems such as $(NH_3)_5Co^{III}-B-Ru^{II}(edta)^+$ and $(NH_3)_5Co^{III}-B-Fe^{II}(CN)_5$ have been reviewed by Haim.[159] This chemistry has been further extended to the study of electron transfer in proteins[160] and through polypeptides.[161]

Late in his professional life, Taube lamented his failure to find evidence for the importance of the electronic factor, a principle that had driven much of his electron-transfer work.

> *"Though I also came under Franck's influence, I had difficulty in overcoming the conviction, largely based on hope, that the electronic factor would play an important role in controlling the rates of all electron-transfer reactions of complex ions. The clarification of the issue, through the work of R. A. Marcus, N. S. Hush, N. Sutin, and others was a great step forward."*[134]

A reexamination of the Taube data in light of later work by Yee et al.[162] leads to the conclusion that the electronic factor is important in these reactions and that Taube had after all found systems in which the electronic factor controlled the rate.[163]

Beginning with the initial experimental results with $Cr^{2+}_{aq}$ mixed with $(NH_3)_5CoCl^{2+}$, these results culminated a remarkable span of accomplishment in defining, in ever more refined detail, the nature of electron transfer in metal complexes. It was this work that led to Henry Taube being awarded the Nobel Prize for Chemistry in 1983. The combination of his experimental work and the theories of Marcus and Hush represent one of the major achievements in chemical research in the 20th century.

## Later Years

Taube was irrepressibly innovative. In his later years in research, he continued to explore coordination chemistry in different guises with an interest in complexes of $V^{II}$,[164−166] substitution and electron transfer in metal complex ion pairs,[167−169] and metallocenes.[170−175] During this period, he also enjoyed consulting at Catalytica,[176−182] where he used his knowledge of chemistry to solve practical problems such as the seminal development of catalysts for methane activation.[183]

## Postscript

Of necessity, this paper reflects the interests of its authors, and the three of us cannot do justice to the full body of Taube's work. We encourage others to write about Taube's work and how he influenced their work and their lives. In addition, this format is a scholarly one, not suitable for affectionate reminiscing about thumb wrestling, record and bottle collecting, thrift-shop purchases, martinis, and bets on five-coordinate Cr. To do justice to that side of Henry's life will require a reunion in the right pub.

Taube loved chemistry and research passionately. When stumped for an explanation of a new result, his style was to gradually back out the laboratory door to retire to his office. He had an insatiable need for new data to the extent that students, to whom he was especially dear, were known to occasionally supply him with fictitious results (to be withdrawn once the master had created a hypothesis about their meaning). His knowledge was encyclopedic. He was enthusiastic and fearless in his scientific endeavors.

## Henry Taube: Master and Inspiration

The impact of Taube and his thinking on modern inorganic chemistry and, in his work on electron transfer, in his definition of one of the fundamental processes of chemistry and biology has been profound. He was admired as a mentor, colleague, and role model for others. In his own words, with his customary, if inaccurate, modesty:

> *"I have always relied on the independence of my coworkers, and to a large extent my contribution to the effort has been that of maintaining continuity."*[24]

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