

# This Week's Citation Classic®

Taube H. Rates and mechanisms of substitution in inorganic complexes in solution.

Chem. Rev. 50:69-126, 1952.

[George Herbert Jones Laboratories, University of Chicago, IL]

Metal-ion complexes differ enormously in the rates at which they undergo substitution, some at rates as slow as those encountered for substitution at carbon, while others undergo changes in composition in the time of mixing the reagents. The significance of this aspect of behavior to the chemistry of the complexes is developed. The distinction between thermodynamic and kinetic stability is stressed. Examples are introduced to show that the rate differences that are noted by no means parallel thermodynamic stability. It is shown that, for complex ions of coordination number six, all those ions that have three and only three d orbitals occupied stand apart as undergoing substitution less rapidly than do those that differ in electronic structure. The correlation is validated by an exhaustive survey of the literature bearing on substitution lability. [The SC<sup>1</sup>® indicates that this paper has been cited in over 300 publications since 1955.]

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My first experience in teaching a course in advanced inorganic chemistry took place at the University of Chicago in the 1946-1947 academic year. I was given complete freedom to choose the subject matter. After having repeated a course devoted to what might be called physical-inorganic chemistry, I decided to try a more descriptive approach and to learn something about coordination chemistry, a subject that I knew to be important but that I had found to be rather boring, at least in the way it was treated in textbooks and review articles then extant.

In the first version of the course, I chose to treat a limited subject area in depth and, because of the large amount of work that had been done in the field, selected the cobaltammines, using the appropriate Gmelin volume both as a source of material and as a guide to the original literature. I had a strong background in principles governing reactivity, in large part as a result of reading the emerging literature devoted to the study of the mechanisms of substitution at carbon, but in part also because of my training.

I was fascinated by the abundance of opportunities there were for applying to the inorganic systems the kind of strategies that had been developed to probe the mechanisms of substitution at carbon. This abundance owed much to the fact that, in contrast to the organic systems, the inorganic realm featured a variety of different centers as the site of substitution. Even when the same ligands are involved, ions of the same oxidation states and similar radii are found to differ enormously in substitution lability, some undergoing substitution so slowly that compositions remain intact on transfer from one phase to another, others responding extremely rapidly to any change in composition or environment. Enough was known about affinities, partly through experimental data gathered in my own laboratories, to convince me that the rate differences could not be understood in terms of thermodynamic stabilities. In discussing rates, differences in ground-state stability are not the relevant parameters, but rather the differences in energy between the ground state and the activated complex. By applying this point of view, I was able to see a correlation between electronic structure and rates of substitution for metal complexes of coordination number six.

This correlation was introduced in the second version of my course on coordination chemistry, but it then rested on an incomplete survey of the literature. It did, however, survive the exhaustive survey I undertook while I was a Fellow of the Guggenheim Foundation, 1949-1950. The results of this survey and the deliberations to which it led were incorporated into the paper that forms the subject of this commentary.

The value of the paper was partly in providing an example of the importance of separating equilibrium stability from kinetic stability in trying to understand reactivity.<sup>1</sup> Though this is an obvious point, the failure to do this clouded the thinking of many at that time. The validity of the correlation itself is independent of theory; it has survived and is by now in the public domain. The paper has a major weakness in that the rationalization of the correlation was done by applying valence bond theory rather than crystal field theory, which was later shown<sup>2</sup> to be a much more satisfactory way for understanding the labilities to substitution of ions of differing electronic structures. [Editor's note: A recent paper on rates and mechanisms of ligand substitutions of technetium<sup>3</sup> is one of many that cite the 1952 paper.]

In my innocence at the time of writing, I didn't know that *Chemical Reviews* was composed of invited papers. Despite the fact that my contribution was volunteered, it was sent out for a review. As a result of the review process, the editors were on the point of rejecting it, but, before they did so, they sent it to Jake Kleinberg, who was then a well-established inorganic chemist. My paper was finally published only because his review was highly favorable. (I learned this from Kleinberg many years later.)

1. Orgel L. E. Effects of crystal fields on the properties of transition metal ions. *J. Chem. Soc.* 1952:4756-61. (Cited 185 times since 1955.)
2. Basolo F & Pearson R G. *Mechanisms of inorganic reactions: a study of metal complexes in solution.* New York: Wiley, 1958. 426 p. (Cited 885 times.)
3. Kido H & Hatakeyama Y. Ligand-substitutional nature of technetium(III). Rate and mechanism of ligand exchange of tris(acetylacetonato)technetium(III) in acetylacetonone. *Inorg. Chem.* 27:3623-5, 1988.