

Geary W J. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds.
Coord. Chem. Rev. 7:81-122, 1971.
[Dept. Chemistry, Sheffield Polytechnic, Sheffield, England]

This review gives the first comprehensive and critical assessment of conductivity data for metal complexes in a variety of non-aqueous solvents, suggests the optimum experimental procedure, and relates the observed experimental values to the nature of the electrolyte in solution. [The SC[®] indicates that this paper has been cited over 630 times since 1971.]

William J. Geary
Department of Chemistry
Sheffield City Polytechnic
Sheffield S1 1WB
England

March 18, 1981

"For several years before 1970 my research group had been investigating transition metal complexes of heterocyclic ligands, particularly from the viewpoint of their possible use as analytical reagents. As so often happens, although this aspect proved to be disappointing another area became of interest. Many of the complexes proved to be coordination polymers, and we became interested particularly in the influence of the ligand structure on that of the complexes. The ligand systems in which we were interested at that time were based on isomers of 1,2-dipyridyl ethylene, and almost without exception the metal complexes they formed were highly insoluble both in aqueous solution and in the common organic solvents.

"This was quite restrictive in terms of the physicochemical methods we could use to investigate the complexes; for instance, our visible spectral data invariably were obtained by diffuse reflectance on solid samples. Partly for this reason, and partly because we were also interested in measuring metalligand formation constants, we started looking at systems which might give soluble (though still polymeric) complexes.

"This was also the period of much work on ligands related to orthophenanthroline, and thus we started looking at metal complexes of dipyridylquinoxalines, which can in some senses be considered as having

two separate phenanthroline coordination systems in the same molecule. We quickly discovered that some of the complexes were indeed soluble in ionizing solvents such as nitromethane, though frequently they decomposed in aqueous media. Thus we were able to start looking at properties of the complexes in solution, particularly to try to relate the structures in solution to those in the solid state. This was where conductivity came in; the method had been used for aqueous solutions of metal complexes from the earliest days of Werner's classical work,¹ but had only recently been extended to nonaqueous solvents.²

"The key requirement is to be able to relate the experimental conductivity value to the electrolyte type, and when we started a literature search to look for reliable reference values we found a bewildering array of so-called correlations. Two lines of approach offered themselves: firstly, to diversify from our main area of interest into electrochemistry, and, secondly, to try a comprehensive and critical review of published data to identify acceptable values.

"At this stage personal factors made the decision for me. I moved from Lanchester Polytechnic in Coventry to Sheffield City Polytechnic, was obliged to live apart from my family for a period, and hence had more free time (particularly in the evenings) than a young family normally allows. Library work and cross-referencing was more amenable to the situation than a new research line, and so the review was written.

"Why has it been so much quoted? I think because it relates to a useful technique in a heavily researched area, and because it isn't just a list of data—it is a critical evaluation of data, with firm proposals for regularising experimental conditions and establishing acceptable reference values of conductivity for coordination compounds. But a chance personal move was the catalyst!

"More recent work is presented in the *Journal of the Chemical Society—Dalton Transactions*.³

1. Werner A & Miolati A. *Z. Phys. Chem.* 12:35, 1893.
2. Gilli N S & Nyholm R S. *J. Chem. Soc.* 1959:3997, 1959.
3. Adam K R, Lindoy L S, Lip H C, Rea J H, Skelton B W & White A H. *J. Chem. Soc. Dalton Trvns.* 1981:74, 1981