This Week’s Citation Classic


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In 1959, when I first became interested in complexes of oxocations, the most extensively studied species was the dioxouranium(IV) or uranyl ion, UO₂²⁺. My first PhD student, Larry Holmes, and I began a brief collaboration at Louisiana State University, on a study of the variation of the symmetric and antisymmetric stretching vibrations of the UO₂²⁺ with different ligands. We established a ligand series that exhibited striking similarities to the well-known spectrochemical ligand series that had generally been generated from optical spectral data. It occurred to me that by studying complexes of molecule-ions, in particular oxocations, we would have more handles on the complexes for studying metal-ligand interactions than there are on complexes of atom-ions. I believed then—and still believe—that perhaps the best, simplest, and most stable and persistent such molecule-ation is VO₂²⁺, oxovanadium(IV) or vanadyl. This species has the added feature of being a “single electron” (d¹ beyond closed shells) electronic system that proved to be a mixed blessing. The very strong, perhaps tripolymerized oxygen, which readily persists in almost all reactions with ligands, permitted observations not possible with complexes of atom-ions.

The most obvious new variable available with an oxometal species was the infrared stretching frequency of the metal-oxygen bond.² This frequency (940-1,020 cm⁻¹) indeed turned out to be sensitive not only to the nature and strength of the equatorial ligands—VO₂²⁺ complexes are nearly always square pyramidal with axial oxygen and with occasional transaxial ligands, but in a few cases are distorted trigonal bipyramidal—but even more sensitive to axial ligands.²,³ Thus the VO₂²⁺ could serve to generate a ligand series based upon the strengthening or weakening of the V-O bond, and the equatorial ligands could serve to enhance either the “softness” or the “hardness” of the central metal species. The presence of a single d electron generated not only experimental studies of electronic spectra and the electron spin resonance (ESR) spectra but several attempts at theoretical treatment of the molecule-ion system. Increasing numbers of single crystal X-ray diffraction studies began to reveal a very short V-O bond length (1.55-1.76 Å), but one that was not too sensitive to the other ligands.

The frequent citation of this paper undoubtedly arose from its critical nature and its timelessness in the mid-1960s. There was rapidly increasing interest in the preparation of new transition-metal complexes and their study by electronic and ESR spectral techniques and in the growing correlation of such data with predictive models, such as ligand field and molecular orbital theories. Adding to its continued frequent citation no doubt is the absence of any more recent general review of VO₂²⁺.

Later work by many others with VO₂²⁺, undiminished in quantity, has largely been more of the same type, simply with new complexes, until the bioinorganic connections and biochemical use of VO₂²⁺ began to be made. Although no more recent general reviews of VO₂²⁺ have appeared since my review, there have been valuable summaries of selected areas of research, such as the inorganic and biochemical aspects of VO₂²⁺ electron paramagnetic resonance spin probes.⁴ The roughly 250 references in this latter review chapter suggest that VO₂²⁺ research is alive and well and occurring in new and exciting areas.