

Selbin J. Oxovanadium(IV) complexes. *Coord. Chem. Rev.* 1:293-314, 1966.
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This paper reviews the flurry of interest surrounding the oxovanadium(IV) species, VO^{2+} , in particular the 70 or so papers published since my more comprehensive review.¹ Complexes of VO^{2+} and their examination by X-ray diffraction, infrared spectroscopy, thermodynamic (stability) studies, electron spin resonance studies, and electronic spectral studies, and attempts at theoretical models, are critically reviewed and updated. [The *SCI*® indicates that this paper has been cited in over 260 publications.]

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In 1959, when I first became interested in complexes of oxocations, the most extensively studied such species was the dioxouranium(VI) or uranyl ion, UO_2^{2+} . My first PhD student, Larry Holmes, and I began a brief collaboration with Sean P. McGlynn, a molecular spectroscopist at Louisiana State University, on a study of the variation of the symmetric and antisymmetric stretching vibrations of the UO_2^{2+} 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 then 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-cation is VO^{2+} , oxovanadium(IV) or vanadyl. This species has the added feature of being a "single electron" (d^1 beyond closed shells) electronic system; that proved to be a mixed blessing. The very strong, perhaps triply bonded, 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 ($940\text{--}1,020\text{ cm}^{-1}$) indeed turned out to be sensitive not only to the nature and strength of the equatorial ligands— VO^{2+} 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 VO^{2+} 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 ($1.55\text{--}1.76\text{ \AA}$), 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 timeliness 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 VO^{2+} .

Later work by many others with VO^{2+} , undiminished in quantity, has largely been more of the same type, simply with new complexes, until the bioinorganic connections and biochemical use of VO^{2+} began to be made. Although no more recent general reviews of VO^{2+} have appeared since my review, there have been valuable summaries of selected areas of research, such as the inorganic and biochemical aspects of VO^{2+} electron paramagnetic resonance spin probes.⁴ The roughly 250 references in this latter review chapter suggest that VO^{2+} research is alive and well and occurring in new and exciting areas.

1. Selbin J. The chemistry of oxovanadium(IV). *Chem. Rev.* 65:153-75, 1965. (Cited 385 times.)
2. Selbin J, Holmes L H & McGlynn S P. Vanadyl complexes. *Chem. Ind.—London* 1961:746-7. (Cited 25 times.)
3. Selbin J & Holmes L H. Complexes of oxovanadium(IV). *J. Inorg. Nucl. Chem.* 24:1111-9, 1962. (Cited 70 times.)
4. Chasteen N D. Vanadyl(IV) EPR spin probes. Inorganic and biochemical aspects. (Berliner L J & Reuben J, eds.) *Biological magnetic resonance*. New York: Plenum Press, 1981. Vol. 3. p. 53-119. (Uncited.)