

Ballhausen C J & Gray H B. The electronic structure of the vanadyl ion.
Inorg. Chem. 1:111-22, 1962.
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The bonding in the molecule $\text{VO}(\text{H}_2\text{O})_5^{2+}$ is described in terms of molecular orbitals. In particular, the most significant feature of the electronic structure of VO^{2+} seems to be the existence of considerable oxygen to vanadium π -bonding. A molecular orbital energy level scheme is estimated that is able to account for both the "crystal field" and the "charge transfer" spectra of $\text{VO}(\text{H}_2\text{O})_5^{2+}$ and related vanadyl complexes. The paramagnetic resonance g factors and the magnetic susceptibilities of vanadyl complexes are discussed. [The *SCI*® indicates that this paper has been cited in over 785 publications.]

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In 1961 I was asked by Bob Parry, the editor of the American Chemical Society's new journal *Inorganic Chemistry*, to contribute a paper to the first issue of the journal. With me in Copenhagen at that time was an eager young postdoctoral fellow, Harry B. Gray. I asked Harry to join forces with me, and we talked about various possibilities. Finally, we settled on the vanadyl project because it was suitable for launching our ideas concerning methods of making an "extended Hückel calculation" for inorganic complexes.

Transition-metal complexes were in those days divided into two classes: the

"classical" Werner complexes and the metallo-organic compounds. We realized that it would require a more general theoretical model to explain the electronic structure of both classes, since large variations in σ - and π -bonding probably occurred. In particular, a framework for the discussion of complexes with strong π -bonding was needed. We wanted to investigate the manifestations of π -bonding in the $(3d)^1\text{VO}(\text{H}_2\text{O})_5^{2+}$ complex using both spectroscopic and magnetic evidence and to combine the findings into a "unified" theory. The outcome was a paper that for the first time combined the crystal field model with the molecular orbital theory, describing both the σ - and π -bonding in this simple Werner complex and identifying the charge transfer states as well as the crystal field states.

The VO^{2+} ion can be bound to a large variety of ligands. In contrast to most d^1 systems, these complexes are quite stable. Using electron paramagnetic resonance spectroscopy, one can therefore study the delocalization of the single electron onto the ligand network, thereby estimating the π -bonding capabilities of the ligand.¹ Our identification of the excited states in the VO^{2+} complexes has never been questioned, and our old paper has become textbook stuff. But, in most cases it is better to quote the original literature than to refer to textbooks, so our paper is cited frequently.^{2,3} It is cited for its treatment of ligand-metal π -interactions, for its treatment of the diagonal elements in a semiempirical molecular orbital calculation of systems with a large degree of ionic character, and because it is the first unified electronic structural model of metal oxo complexes.

1. Satyanarayana N & Radhakrishna S. EPR and electronic absorption studies of vanadyl ions in the $\text{Cd}(\text{NH}_3)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ single crystals. *J. Chem. Phys.* 83:529-34, 1985.
2. Penner-Hahn J E, Benfatto M, Hedman B, Takahashi T, Donisch S, Groves J T & Hodgson K D. Polarized x-ray absorption near-edge structure of highly oxidized chromium porphyrins. *Inorg. Chem.* 25:2255-9, 1986.
3. Che C-M, Lai T-F & Wong K-Y. Synthesis, reactivities, and structural studies on high-valent ruthenium oxo complexes. Ruthenium(IV), ruthenium(V), and ruthenium(VI) oxo complexes of tertiary amine ligands. *Inorg. Chem.* 26:2289-99, 1987.

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