

Addition to Vanadocene *de Novo*: Spectroscopic and Computational Analysis of Bis(η^5 -cyclopentadienyl)vanadium(II)

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In the course of work on other paramagnetic metallocenes, we discovered that we had neglected to point out that vanadocene (VCp₂) in solution and in a variety of solid hosts was extensively investigated by Ammeter using X-band EPR.¹ His results on VCp₂ are summarized in Table 2 of this paper,¹ which includes data on a wide variety of other paramagnetic [MCp₂]⁰⁺ (M = Mn^{II}, Fe^{III}, Co^{II}, Ni^{III}) species, including “sandwich” type complexes with other aromatic ligands such as MeCp[−] (methylcyclopentadienide anion) and carboranes (C₂B₉H₁₁[−], C₂B₉H₁₀Ph[−]). This paper is highly recommended to those interested in paramagnetic sandwich complexes.

Specifically concerning VCp₂, Ammeter’s results on this complex in 2-Me-THF solution at 4 K agreed with those recorded at 77 K by both Prins et al.^{2,3} and ourselves.⁴ Ammeter also obtained EPR spectra for VCp₂ in the following diamagnetic hosts: FeCp₂, MgCp₂, Mg(MeCp)₂, and Cr(η^6 -C₆H₆)₂.¹ The variation in spin Hamiltonian parameters among these is nearly within experimental error, $g_{\perp} = 1.988(4)$, $g_{\parallel} = 2.000(15)$, $A_{\perp}(^{51}\text{V}) = 62.4(6)$ MHz, and $A_{\parallel}(^{51}\text{V}) = 108(1)$ MHz, and is essentially the same as the collection of frozen solution results.^{1–4} We thus believe that the zero-field splitting (zfs) parameters we obtained by high-frequency and -field EPR (HFEPR) spectroscopy in toluene frozen solution would be virtually the same in such diamagnetic hosts and are thus truly characteristic features of vanadocene.

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