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EPR Characterization of V(IV) Complexes with and without an oxo group

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Outline

- Introduction to EPR
- EPR of V(IV) in fluid solution
  - Speciation in reactions
- EPR of V(IV) in glassy solution
  - Interpretation of hyperfine coupling constants
- Tumbling correlation times
- Electron spin relaxation times
  - Impact of flexibility
- Electron-nuclear double resonance to measure small couplings
- V(III) requires high magnetic fields

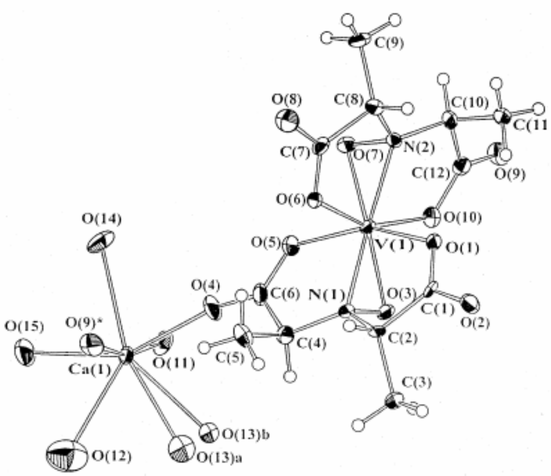
V(IV)

V(IV) is d_{xy}^1.

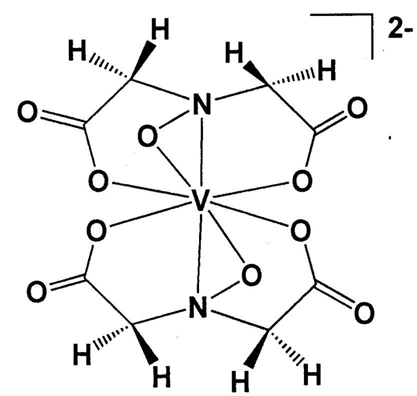
One unpaired electron gives S = ½

Most EPR studies have been performed on complexes of VO^{2+}

The natural product amavadin and its analogs are air-stable V(IV) complexes without an oxo group.

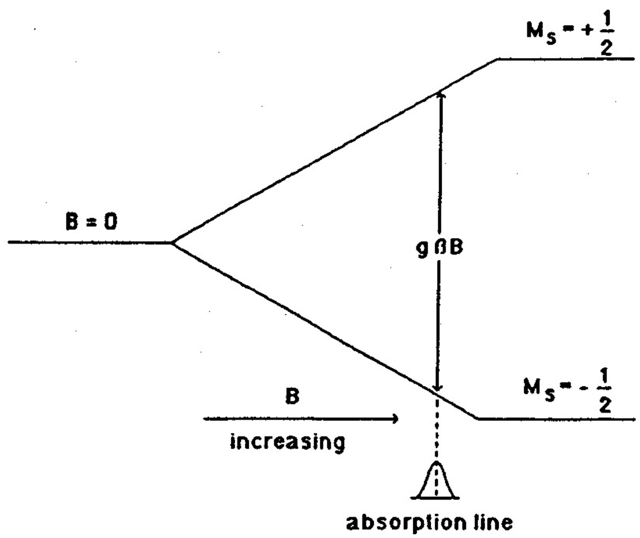


Amavadin bound to Ca^{2+} cation



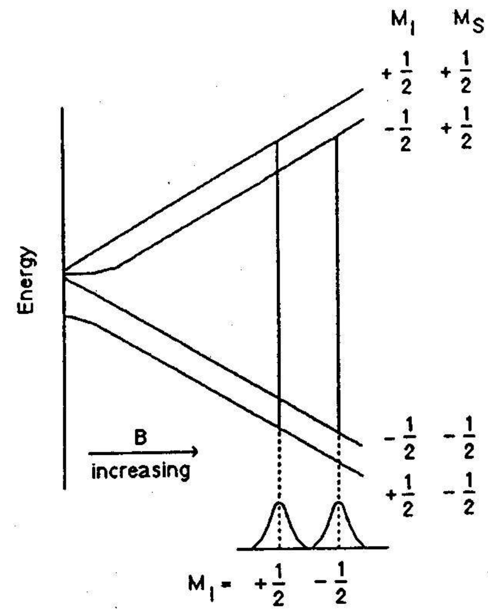
$Ca(H_2O)_5[V^{IV}(hida)_2]. H_2O$

EPR Basics



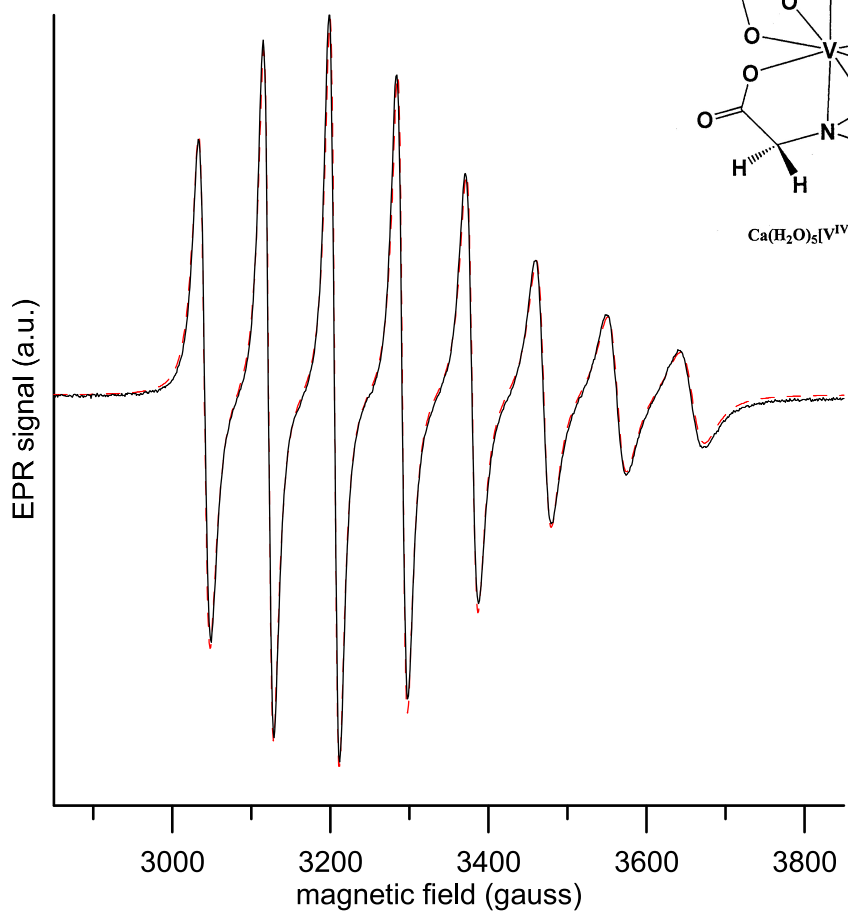
$h\nu = g\beta B$

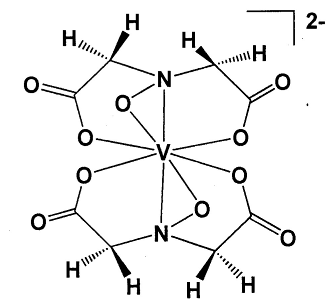
EPR spectra usually are displayed as the 1st derivative of the absorption signal.



The number of hyperfine lines is 2nI+1.

V(IV) in H_2O at 295 K





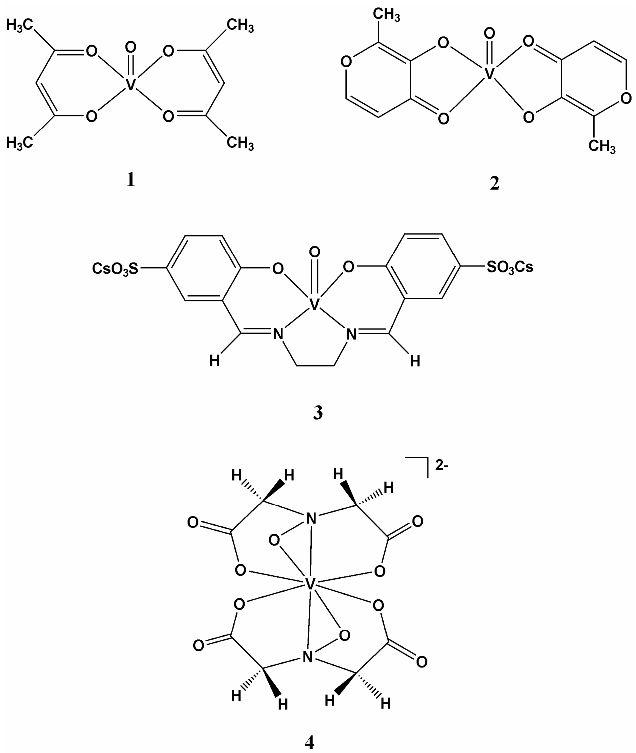
$Ca(H_2O)_5[V^{IV}(hida)_2]. H_2O$

The hida complex is a model for the natural product amavadin. Note that it is V(IV) complex, but without an oxo group!

Vanadium nuclear spin = 7/2
2nI + 1 lines = 8

Parameters from simulations
g_{iso} = 1.964
A_{iso} = 81.3 x 10^{-4} cm^{-1}

Comparison of g_{iso} and A_{iso} values in H_2O



Compound	g_{iso}	A_{iso}
1 $VO(acac)_2$	1.966	91
2 $VO(maltol)_2$	1.963	95
3 $VO(salen\text{-}SO_3)^{2-}$	1.963	85
4 $V(hida)_2^{2-}$	1.964	81

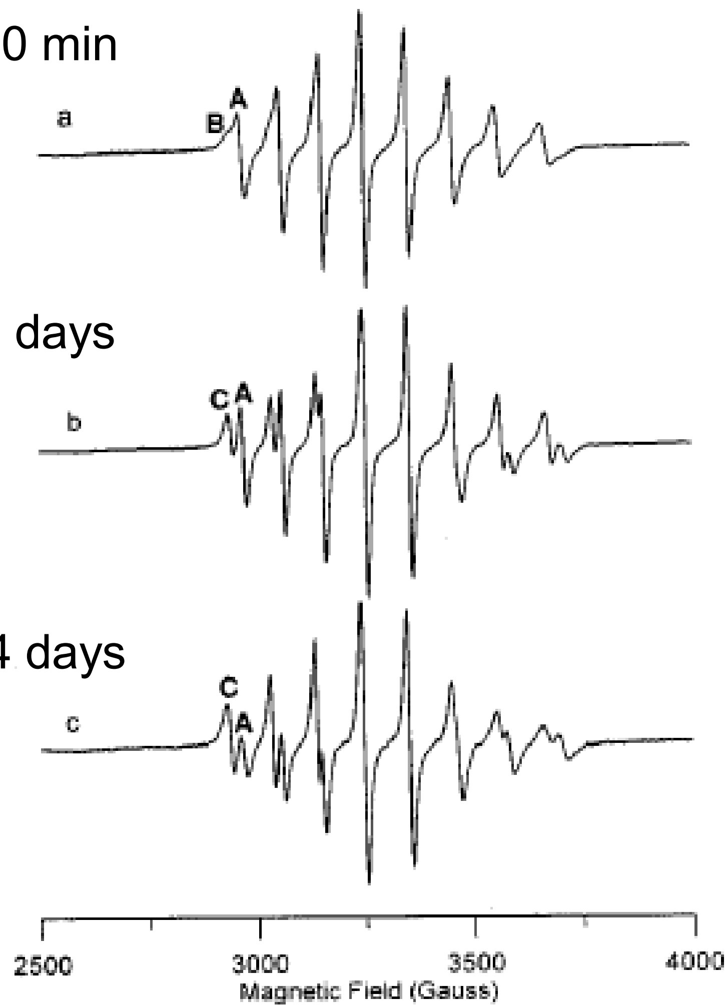
- g-values ~ 1.965 are typical for V(IV)
- variations in A_{iso} are larger than for g_{iso}
- A_{iso} and g_{iso} for $V(hida)_2^{2-}$ are similar to those for oxo complexes

Differences in A_{iso} are large enough to monitor reactions of $VO(acac)_2$ in H_2O

t = 10 min

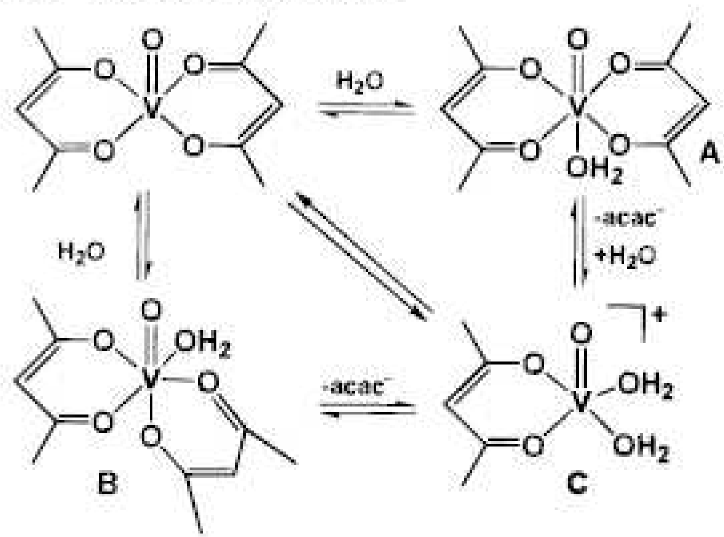
t = 2 days

t = 24 days



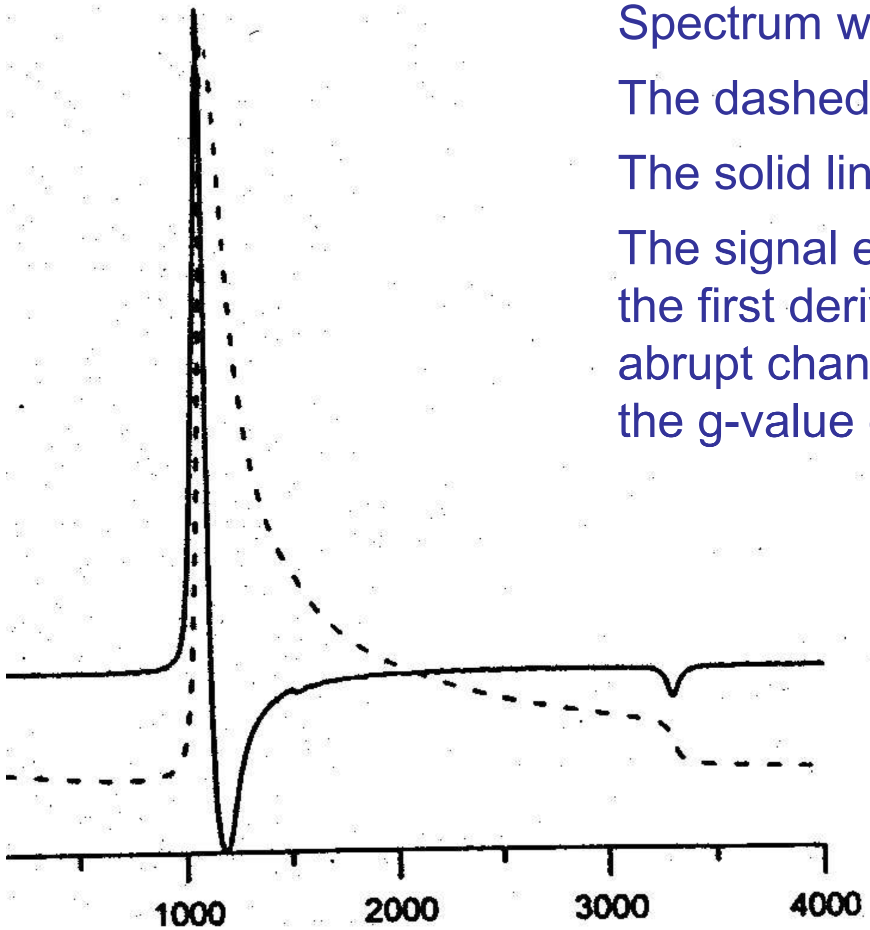
The proposed assignments of species A, B, and C are:

Scheme 1. Species A, B, and C



Amin et al., Inorg. Chem. 39, 406 (2000).

Anisotropy in immobilized samples



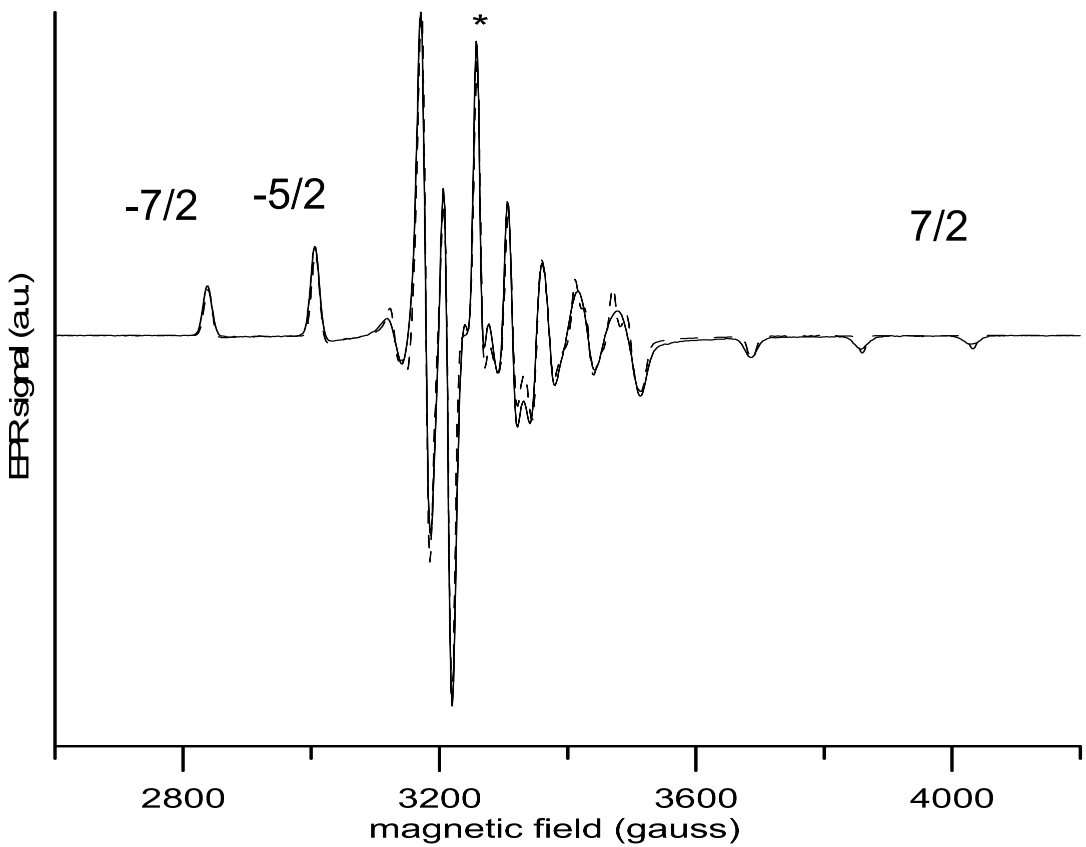
Spectrum with $g_x = g_y = 6.0$, $g_z = 2.0$.

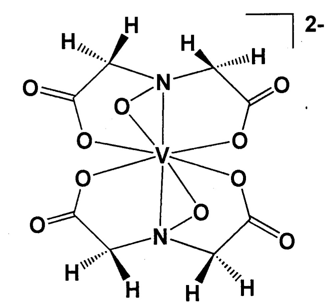
The dashed line is the absorption curve.

The solid line is the first derivative.

The signal extends from 1000 to 3300 G but the first derivative display emphasizes the abrupt changes in amplitude that occur near the g-value extrema.

Rigid-lattice spectra at 118 K





$Ca(H_2O)_5[V^{IV}(hida)_2].H_2O$

X-band spectrum in 1:1 water:glycerol, which forms a glass.

Parameters from simulations:

g_x= 1.986, g_y= 1.984, g_z= 1.918

A_x = 42, A_y = 49, A_z = 153 x 10^{-4} cm^{-1}

Comparison of g and A values in glassy 1:1 water:glycerol

Sample	g_x, A_x	g_y, A_y	g_z, A_z
$VO(maltol)_2$	1.977 60	1.974 55	1.939 169
$VO(acac)_2$	1.980 54	1.967 56	1.950 163
$VO(salen\text{-}SO_3)^{2-}$	1.978 46	1.974 55	1.955 154
$V(hida)_2^{2-}$	1.986 42	1.984 49	1.918 153

Units for A values are 10^{-4} cm^{-1}

To avoid aggregation and locally high concentrations it is important to use solvents that form a glass when cooled.

Interpretation of $A_{||}$ values

- For square pyramidal vanadyl complexes the additive contributions to $A_{||}$ from various ligands have been tabulated. Contributions decrease in the order
  $H_2O > Cl^- > py > OH^- > RO^- > RS^-$
  T. S. Smith et al., Coord. Chem. Rev. 228, 1 (2002).

- For π-bonding ligands, such as imidazole, the contribution to $A_{||}$ increases as the angle between the ligand plane and vanadyl bond increases. T. S. Smith et al., Coord. Chem. Rev. 228, 1 (2002).

- DFT calculations have improved substantially. Values of A_{iso} and $A_{||}$ for vanadyl complexes can be calculated within about 10%. A. C. Saladino and S. C. Larsen, J. Phys. Chem. A 107, 1872 (2003)

Impact of tumbling correlation time for $V(hida)_2^{2-}$