High-Field EPR and Relativistic DFT Studies on the Complexation of Pb(II) Ions with Semiquinone Radicals and with Natural Humic Acids

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Introduction

Humic acids (HA), which are major components of humic substances, contain semiquinone radicals in equilibrium with structural polyphenol and quinonoid moieties, providing donor atoms able to coordinate metal ions [1]. The radical composition and their g values were extensively studied using EPR to detect various processes responsible for organic matter transformations [2]. Interaction of Pb^{2+} with humic acids results in formation of new semiqinone radicals characterized by unusual g values [2]. Small g anisotropy leading to broad and unstructured lines, as well as overlap with spectra of the parent radicals prevents determination of g matrix components from X-band EPR.

Experimental

Humic acids were extracted from various sources, like compost (CHA) and peat (PHA). Pb-3,4-DHBA (**1** and **2**) were precipitated from water solution containing lead acetate and 3,4 DHBA (molar ratio=1:2 for**1** and 1:3 for **2**). High-field EPR spectra at frequencies larger than 400 GHz were recorded on the transmission instrument at the NHMFL EMR facility.

Results and Discussion

g-tensor components were determined for naturally occurring and model semiquinones from 3,4-dihydroxybenzoic acid=3,4-DHBA) as well as their Pb(II) complexes [Fig. 1]. The agreement between the experimental and theoretical g parameters is the fundamental criterion for verification of DFT calculations predicting geometry [3] electronic structure, acid-base equilibrium [3], metal ion complexation ability, and solvent effects. The calculated *g* parameters for $[Pb(H_2L)_2]^{\bullet+}$, L=3,4-DHBA, g_1= 2.0055, g_2=2.0036, g_3=2.0015, are in a great agreement with the experimental values g_1=2.0065, g_2=2.0028 and g_3= 2.0017. The $[Pb(H_2L)_2]^{\bullet+}$ model mimics very well the properties of the radical complexes. These results allowed to propose the interaction diagram of molecular orbitals for formation of $[Pb(H_2L)_2]$ complex and its oxidation to $[Pb(H_2L)_2]^{\bullet+}$ radical complex.

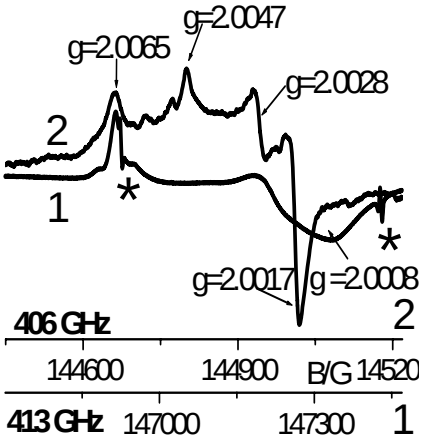

Fig. 1. Powder HFEPR spectra of complexes formed in Pb-(3,4-DHBA) systems **1** and **2**; *****-standard

Conclusions

HFEPR studies appeared to be the only method for determination of g-tensor components which values allowed for verification of theoretical g-tensor parameters and hence electronic and molecular structure of Pb(II) complexes with humic acids and their models, calculated using DFT.

Acknowledgements

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References

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