Influence of Pb(II) Ions on the EPR Properties of the Semiquinone Radicals of Humic Acids and Model Compounds: High Field EPR and Relativistic DFT Studies

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Introduction
The interaction of humic acids (HAs) with metal ions is particularly important as HAs together with clays and metal oxides are a key factor determining the metal binding in soils [1]. Significant changes in the free radicals concentration resulting from the interaction of HAs with metal ions were observed, e. g. with Mg$^{2+}$, Cu$^{2+}$, Ca$^{2+}$, Zn$^{2+}$, or Cd$^{2+}$. However, a completely different effect is observed for Pb$^{2+}$ ions. The complexation of Pb$^{2+}$ with HA macromolecules leads to formation of a new kind of stable radical species characterized by unusually low $g$ values ($g \approx 2.001$) [2,3].

Experimental
High-field and frequency EPR spectra (416.00 GHz) were recorded on the transmission instrument at the NHMFL EMR facility. All computations were performed by using the ADF suite of programs [4] as described in ref. 5.

Results and Discussion
The formation of Pb(II) complexes with the model radicals derived from 3,4-dihydroxybenzoic acid (34dhb) was accompanied by a significant decrease of $g$ as compared to the parent radicals. The Density Functional Theory calculations, including prediction of the $g$ tensors, were carried out for complexes with different forms of model radical ligands (L$^{2-}$, HL$^{-}$, and H$_2$L$^-$) representing various ligation schemes and protonation states. It was shown that the structures with a significant accumulation of spin population on the Pb atom cannot explain the experimentally observed $g$ tensor component shifts.

Conclusions
The determination of the $g$ tensor components for model systems was possible only from high-frequency and high-field EPR measurements (Fig. 1) at low temperatures. Formation of two complexes was revealed by two different high-field EPR spectra characterized by dissimilar $g$-tensor patterns. For one of them, the splitting due to an anisotropic hyperfine interaction with the $^{207}$Pb nucleus (71.6 G) was observed. The comparison of the computed and experimental $g$ tensor components indicates that only the decrease of spin population on all oxygen atoms accompanied by a corresponding spin population increase on the carbon atoms of the benzoic ring can reproduce the experimental results (Fig. 2), thus supporting strongly the prediction of the Pb(II) complex geometry in [5].

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References