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EPR AND DFT STUDIES ON HETEROMETALLIC POLYNUCLEAR COMPOUNDS AND Pb(II) COMPLEXES WITH SEMIQUINONE RADICALS.

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Applications of High-Field and High-Frequency EPR (HF EPR) to study the nature of anisotropic exchange interactions between the paramagnetic centers present in different hetrometallic systems, in correlation with their isotropic exchange interactions of different character and crystal and molecular structure, are reviewed. The report presents also the results of the DFT calculations of geometry, g parameters and distribution of unpaired electron density performed to explain the significant effects of Pb(II) ions on natural and model semiquinone radicals, which are pronounced in the changes of EPR spectral properties.

INTRODUCTION

Heterometallic compounds exhibit important properties which make them useful as new magnetic materials, catalysts, electrical conductors and electron-transmitters. Polynuclear complexes involving organic spacers between metal ions play crucial roles in biological systems which contain exchange-coupled paramagnetic metals. Among them are dicopper enzymes e.g. hemocyanin and dimanganese enzymes, e.g. arginase (Makhankova, Beznischenko, Kokozay, Zubatyuk, Shishkin, Jezierska, Ozarowski, 2008 and references therein). This report presents review of HF EPR studies of anisotropic exchange interactions in heteronuclear systems containing exchange coupled paramagnetic ions in dimeric, tetrameric, and hexameric complexes. The applications of HF EPR technique and DFT calculations to investigate, experimentally and theoretically, respectively, the g tensor components of the semiquinone radicals and their complexes with Pb(II) are also presented. The semiquinones are most widespread free radicals formed in various biopolymers, e.g. humic acids (Witwicki, Jerzykiewicz, Jaszewski, Jezierska, Ożarowski, 2009).

RESULTS AND DISCUSSION

Polynuclear heteromettallic compounds

An unique one-step synthesis (based on reaction of zerovalent metal, another metal oxide or salt, atmospheric dioxygen and organic polyfunctional ligand in a solution) allowed to prepare a variety of heterometallic compounds with unexpected and unusual structures (Makhankova, Vassilyeva, Kokozay, Reedijk, van Albada, Jezierska, Skelton, 2002; Buvaylo, Kokozay, Vassilyeva, Skelton, Jezierska, Brunel, Ozarowski, 2005a; Buvaylo, Kokozay, Vassilyeva, Skelton, Jezierska, Brunel, Ozarowski, 2005b; Buvaylo, Kokozay, Vassilyeva, Skelton, Eremenko, Jezierska, Ożarowski, 2009; Makhankova *et al*., 2008; Semenaka, Nesterova, Kokozay, Dyakonenko, Zubatyuk, Shishkin, Boca, Jezierska, Ozarowski, 2010).

The following polynuclear heteromettallic compounds were chosen to demonstrate the correlations between magnetic iso- and anisotropic exchange interactions and geometric properties, determined from the temperature dependence of magnetic susceptibilities, EPR spectra and crystal structure, respectively:

a) two complexes containing cyclic tetrameric cations $[Cu_2Co^{III}_2(H_2L)_2(L)_4]X_2{\cdot}(Solv)n$ (**1**) Makhankova *et al.*, 2002) and $[Cu_2Zn_2(NH_3)_2Br_2(HL)_4]Br_2{\cdot}CH_3OH$ (**2**) (Buvaylo *et al.*, 2005a), {H_2L=diethanolamine}, with antiferromagnetic interaction through a –O-Zn-O–

bridge in (**2**) (J=35.0 cm^{-1}, $H=J\mathbf{S_1}\cdot\mathbf{S_2}$), in contrast to negligible interaction through –O-Co-O- bridge in (**1**).

b) [$Cu_4(NH_3)_4(HDea)_4$][$CdBr_4$]$Br_2$3dmf·H_2O, (H_2Dea = diethanolamine), (**3**) (Buvaylo *et al.,* 2005b), containing a tetrameric cubane cation (ferromagnetically coupled with J= -65cm^{-1}, S=2 ground state)

c) [$Cu_6(HTea)_6Cd_2I_4$]·4dmf, (H_3Tea=triethanolamine), (**4**) (Buvaylo *et al.,* 2009) forming hexa-cooper chain linked by alkoxo bridges, with central Cu-Cu pair involved in ferromagnetic interaction (J= -57 cm^{-1}, S=1 ground state).

d) [$Cu(en)_2$][$Mn_2(succ)_2Cl_2$], (succ=succinate), (**5**) (Makhankova *et al.,* 2008), with a "lantern" structured anion and containing antiferromagnetically coupled Mn-Mn pairs ($J_{Mn\text{-}Mn}$=31cm^{-1}, S=1 ground state), substituted by a small amount of Mn-Cu pairs ($J_{Mn\text{-}Cu}$= 8 cm^{-1}, S=2 ground state).

e) Two new macrocyclic tetranuclear complexes with all metal ions in one plane, $Zn_2Cr_2(NCS)_4Dea)_2(HDea)_2$]) 4dmso (**6**) and [$Zn_2Cr_2(NCS)_4(Dea)_2(HDea)_2$] 2$CH_3CN$ (**7**), (Semenaka *et al.,* 2010), which show weak antiferromagnetic coupling between chromium centers with J=13.7 cm^{-1} and J = 9.4 cm^{-1}

HF EPR spectroscopy was applied as irreplaceable method to gain insight into the specificity of anisotropic exchange between paramagnetic metal centers involved in the heterometallic complexes.

Only HF EPR spectra exhibited very well resolved resonances due to three excited spin states S=1, 2, 3 for compounds (**6**) and (**7**) depending on temperature (Fig.1).

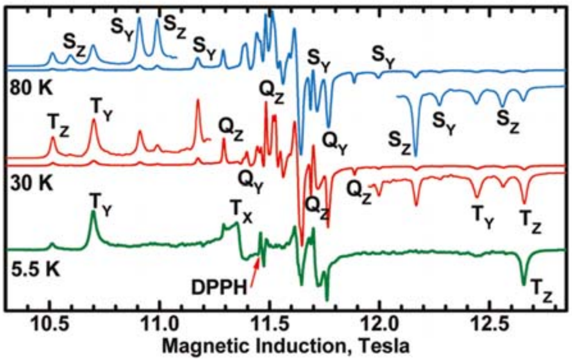

Fig.1. Powder EPR spectra of compound (**6**) at 321.6 GHz. The temperature dependencies allowed assign transitions to the triplet, quintet, and septet spin states (S=1-3, marked with T, Q, and S, respectively) and determine the sign of the ZFS parameters in each spin state. X, Y, and Z indicate the molecular orientations for respective resonances. (Semenaka *et al.,* 2010).

The HF EPR spectra were interpreted using an orthorhombic symmetry spin Hamiltonian:

$$\mathbf{H} = \mu_B\mathbf{B.g.S} + D[\mathbf{S}_z^2\text{-}S(S+1)/3] + E(\mathbf{S}_x^2\text{-}\mathbf{S}_y^2)$$

The Zeeman $\mathbf{g_i}$ factors and the zero-field splitting (ZFS) parameters D and E were determined by fitting simultaneously dependences of the resonance fields for all observed signals versus the microwave frequency over the range 52–413 GHz as is exemplified in Figure 2 for compound (**5**) (Makhankova *et al.*, 2008).

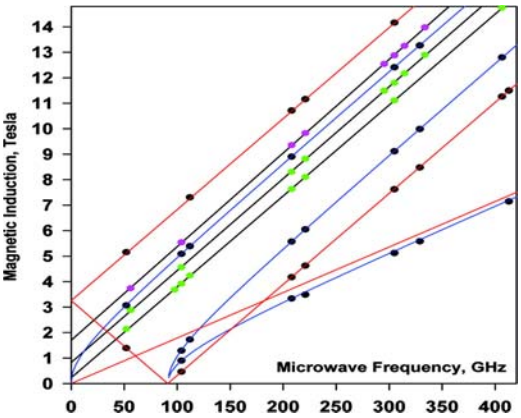

Fig. 2. Frequency dependencies of the EPR signals observed for compound (**5**). Black dots represent experimental resonances at 30 K assigned to the triplet ground state of the Mn-Mn pairs; solid lines are the resonances calculated for S = 1, $g_x = g_y = g_z$ =2.00, D =−3.046 cm^{-1} and E = 0. Color dots represent resonances due to the Cu-Mn impurity pairs with S=2, observed down to 3 K. (Makhankova *et al.*, 2008)

The sign of D could be determined due to the peculiar intensity pattern in the low-temperature spectra, where the combined effect of the zero-field splitting and

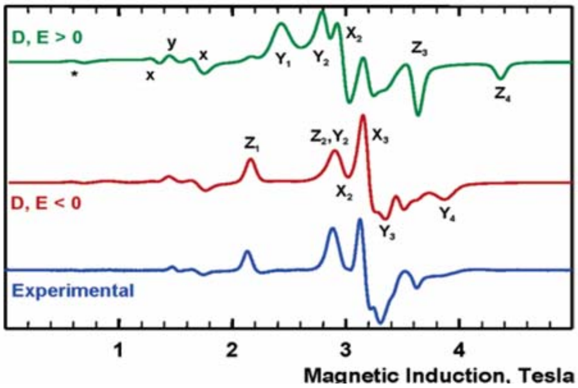

Fig. 3. Experimental EPR spectrum of compound (**3**) at 4.0 K and 93.654 GHz (bottom) and spectra simulated with either D= -0.3529 cm^{-1} and E= -0.0469 cm^{-1} or D= +0.3529 cm^{-1} and E= +0.0469 cm^{-1}. Boltzmann population of the M_S levels at low temperature affects the EPR resonance intensities, allowing determination of the sign of D. Capital letters X, Y, and Z indicate the orientations of the magnetic field at which the respective "allowed" transitions occur. Small letters indicate the "forbidden" transitions (Buvaylo *et al.,* 2005).

Zeeman splitting is comparable to the thermal energy, kT. Temperature dependences of the resonances allowed to detect the transitions within various spin states of the coupled systems (presented in Figure 3 for $[Cu_4(NH_3)_4(HL)_4][CdBr_4]Br_2 3dmf{\cdot}H_2O$ (**3**))

The determination of three contributions to the experimental ZFS parameters (D_{exp} and E_{exp}), i.e. the magnetic dipole-dipole (d-d) interactions, anisotropic exchange (ex) interactions and ZFS parameters of individual ions ($D_1=D_2$, $E_1=E_2$) in $[Cu(en)_2][Mn_2(succ)_2Cl_2]$ (**5**) is shown here as an example (Makhankova *et al.*, 2008)

$D_{12} = D_{d\text{-}d} + D_{ex}$, $E_{12} = E_{d\text{-}d} + E_{ex}$,

$D_{ex} = \alpha_S D_{12} + \beta_S (D_1 + D_2)$, $E_{ex} = \alpha_S E_{12} + \beta_S (E_1 + E_2)$,

where: eg. α_S and β_S are 3.7 and –3.2, respectively in the S = 1 state. (Bencini, Gatteschi, 1990)

Since $D_{d\text{-}d} = -3g^2\mu_B^2/r^3$, we obtain –0.17 cm^{-1} for $r_{Mn\text{–}Mn}$ = 3.11 Å.

The dipolar contribution to $D_{S=1}$ is 3.7·(–0.17) cm^{-1} = –0.63 cm^{-1}. Neglecting the unknown and presumably small contribution due to anisotropic exchange interactions (because of the weak isotropic exchange), one can estimate the $D_1 = D_2 = D_{Mn}$ parameter for separate Mn(II) ions: D_{Mn} = [–3.05–(–0.63)]/(–6.4) = +0.38 cm^{-1}. D_{Mn} was predicted theoretically by using the ab-initio/DFT ORCA software package. The X-Ray structure of the dimanganese unit was used in which one Mn(II) was replaced by Zn(II). The calculated parameters, D = +0.312 cm^{-1}, E/D = 0.015, are close to the single-ion parameters D_{Mn} determined here.

Pb(II) complexes with semiquinone radicals

X-band (9.76 GHz) and HF (416.00 GHz) EPR was used (Fig. 4) to study the interactions between metal ions and semiquinone radicals of natural humic acids (HA) and their simple models (Witwicki *et al.*, 2009). The formation of Pb(II) complexes with the radicals was accompanied by an apparent decrease of g_{av} parameters as compared to those for parent radicals (g=2.0012 for the Pb(II)-radical complex in Pb-HA system compared to g=2.0033 for the radicals in HA observed at X-band EPR). Two types of the complexes were identified depending on the initial concentration of Pb(II) ions. For one of them the anisotropic hyperfine coupling with the ^{207}Pb nucleus was observed (Fig. 4).

Systematic DFT calculations were carried out for Pb(II) complexes with various forms of the radical ligands ($L^{2-\bullet}$, $HL^{-\bullet}$, and $H_2L^{\bullet}$) derived from 3,4-dihydroxybenzoic acid (34dhb), representing different coordination schemes. The g_i parameters calculated for the structure characterized by a significant accumulation of the spin density on the Pb atom deviate strongly from the g_i values observed experimentally. The calculations have indicated that only the decrease of spin population on all oxygen atoms accompanied by spin population increase on the carbon atoms of benzoic ring can reproduce the experimental results and most likely is responsible for the observed shifts of g-tensor components. This was predicted for the structure in Figure 5, in which the lead atom is bound via carboxyl oxygen atoms and both hydroxyl oxygen atoms are protonated.

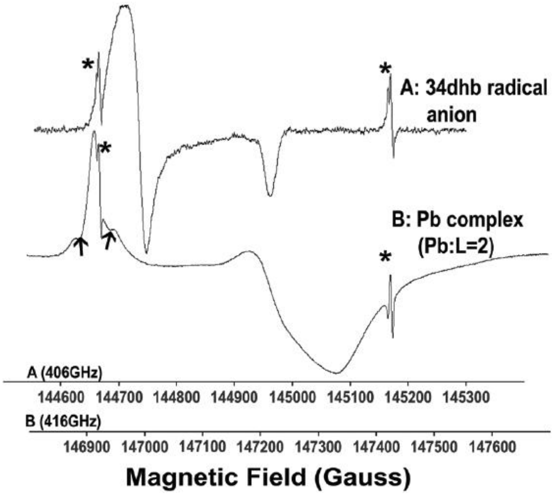

Fig. 4. High field (416 GHz) EPR spectra recorded at 10 K for the **34dhb radical anion** (spectrum A, frozen alkaline water solution with g_x=2.0062, g_y=2.0057, g_z =2.0026 and spectrum B for one **complex formed in Pb-34dhb** powder system with g_x=2.0065 g_y=2.0028, g_z=2.0008). Asterisks: signals of a standard (H-atoms in octaisobutyl-silsesquioxane, g= 2.00294, A=505.5 G). The arrows point towards the 'perpendicular' hyperfine components due to the ^{207}Pb nucleus (I=1/2, 22.1% abundance) (Witwicki *et al.*, 2009).

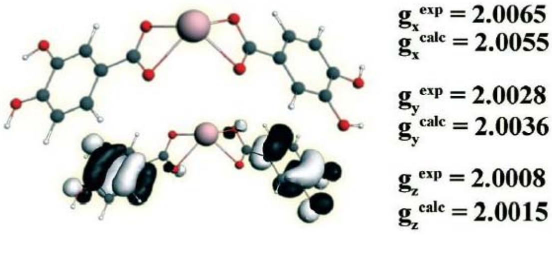

Figure 5. The structure of Pb(II) complex with 34dhb radicals that properly predicts g-tensor components and Singly Occupied Molecular Orbitals (SOMO) isosurface (0.03 a.u.) calculated at the VWNBP86/TZP level (Witwicki *et al.*, 2009).

The reaction mechanism leading to the Pb(II)–radical complex includes two steps: formation of diamagnetic Pb(II) and 34dhb complex and its oxidation into radical form has been also theoretically proposed.

The geometries were optimized and **g** tensors calculated with Amsterdam Density Functional (ADF) version 2007 using zeroth-order regular approximation (ZORA), built-in Slater-type ZORA TZP basis set and local spin density approximation by Vosko, Wilk and Nursai (VWN) with Becke's exchange and Perdew's correlation functionals (BP86).

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