Structural and HFEPR Studies on Polynuclear Ni/Zn Schiff-Base Complexes

Vassilyeva, O.Yu., Kasyanova K.V., Buvaylo E.A. (Taras Shevchenko U., Ukraine, Chemistry); Ozarowski, A. (NHMFL)

Introduction

The current project is devoted to the synthesis of novel transition metal complexes of Schiff base ligands and their characterization by spectroscopic methods and X-ray crystallography. In the present work, three new Ni/Zn heterometallic complexes $[NiZnL'_2(OMe)Cl]_2$ (**1**), $[NiZnL''DeaCl]_2$ (**2**) and $[Ni_2(H_3L''')_2(o\text{-Van})(CH_3OH)_2]Cl\cdot[ZnCl_2(H_4L''')(CH_3OH)]\cdot 2CH_3OH$ (**3**) were synthesized in a coordination-driven self-assembly processes. L', L'' and L''' are the multidentate Schiff base ligands, which are condensation products of *o*-vanillin (*o*-VanH) with CH_3NH_2, NH_2OH, and aminopolyol, respectively. Structure of the dimeric complex $[NiZnL''DeaCl]_2$ (**2**) is shown in **Fig.1**.

Fig.1 Structure of $[NiZnL''DeaCl]_2$
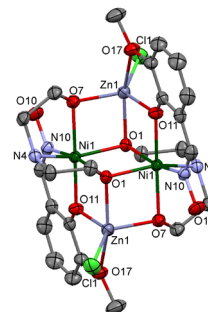
Experimental

The HFEPR spectra of powder samples were recorded on the 15/17 T SC magnet and transmission spectrometer of the EMR facility at temperatures from ca. 3 K to 30 K, microwave frequencies 60−640 GHz and magnetic fields up to 14.9 T. A HFEPR spectrum of **2** is presented in **Fig.2**.

Results and Discussion

Magnetic susceptibility measurements revealed that complexes **1** and **3** are weakly antiferromagnetic, while **2** is weakly ferromagnetic. HFEPR spectra of an $S = 2$ state resulting from exchange interactions between the two Ni^{2+} ($S = 1$) ions were observed in all three cases. Because of the small exchange integrals ($J = -6.5$ cm^{-1} for **2**), the Giant Spin model could not be successfully employed. The spectra were thus simulated using the microscopic spin Hamiltonian [1]

$$\hat{H} = J\hat{S}_1\hat{S}_2 + \mu_B B\{g_1\}(\hat{S}_1 + \hat{S}_2) + D_{Ni}\left\{\hat{S}_{z1}^2 - \frac{1}{3}S(S+1)\right\} + E_{Ni}\left(\hat{S}_{x1}^2 - \hat{S}_{y1}^2\right) + D_{Ni}\left\{\hat{S}_{z2}^2 - \frac{1}{3}S(S+1)\right\} + E_{Ni}\left(\hat{S}_{x2}^2 - \hat{S}_{y2}^2\right) +$$
$$D_{12}\left\{\hat{S}_{z1}\hat{S}_{z2} - \frac{1}{3}\hat{S}_1\hat{S}_2\right\} + E_{12}\left(\hat{S}_{x1}\hat{S}_{x2} - \hat{S}_{y1}\hat{S}_{y2}\right)$$

[1]

Large, negative D_{Ni} of -4.5 cm^{-1} and $E_{Ni} = -0.80$ cm^{-1} were found, while the anisotropic interaction parameters D_{12} and E_{12} were very small, about 0.02 cm^{-1}. "Broken symmetry" Density Functional Theory calculations were performed. The resulting J values for **1** – **3** were in reasonable agreement with the experimental data. Theoretical calculations of the D_{Ni} parameters are being performed.

Conclusions

The generation of the ligands *in situ* along with the use of a zerovalent metal as a source of one kind of metal ions [1] afforded the reaction systems with complex equilibria between several components that eventually released **1, 2** and **3** as the most stable assemblies. The first two complexes are symmetric dimers with a $Ni_2Zn_2O_6$ central core and Ni⋯Ni distances of 3.220 and 3.146 Å, respectively. The third compound is a novel heterometallic cocrystal salt solvate built of alternating sheets of a neutral zwitterionic Zn^{II} Schiff base complex and of ionic salt containing dinuclear Ni^{II} complex cations. The phenolate-bridged Ni atoms in the cation of **3** are separated at 3.33 Å. The cation lacks crystallographic symmetry.

A rare success in interpreting EPR spectra of dinuclear nickel(II) complexes [2] was achieved, which was only possible thanks to the HFEPR. The results of this work are currently being prepared for publication.

Fig.2 EPR spectrum of **2** at 6 K, 295.2 GHz. Red trace was simulated using spin Hamiltonian [1].

Acknowledgements

References

[1] Buvaylo, E.A., *et al*., Cryst. Growth Des., **12**, 3200−3208 (2012).
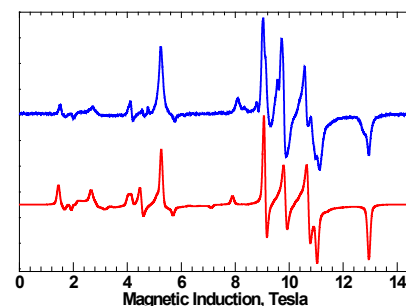[2] Herchel, R., *et al*., J. Am. Chem. Soc., **129**, 10306–10307 (2007).