Introduction

The complex of *E. coli* Glx1 enzyme with Ni$^{2+}$ is involved in the first step of the detoxification of cytotoxic pyruvaldehyde. The mononuclear nickel center similar to that of Glx1 was found in the nickel-sensing NmtR repressor from *Mycobacterium tuberculosis*. The nickel ion in this protein is thought to be coordinated to oxygen and nitrogen ligands in a pseudooctahedron, the UV-Vis absorption spectrum confirms such coordination. In order to mimic the coordination surrounding of Ni(II) ion in Glx1, we have employed two biologically important compounds - 9,10-dihydro-9-oxo-10-acridineacetic acid (CMAH), a powerful interferon inducer, and imidazole. CMAH delivered carboxylate group for binding Ni(II), while the imidazole molecule was used to model histidine residues in the nickel containing proteins.

Experimental

Magnetic susceptibility down to 1.9 K at 500 mT and magnetization up to 5 T at 1.9 K were measured with a Quantum Design SQUID magnetometer. Low-temperature HFEP spectra were recorded at the EMR facility of the NHMFL over the frequency range 52–432 GHz with magnetic fields up to 14.5 T. Detection was provided by an InSb hot-electron bolometer (QMC Ltd., Cardiff, UK). Magnetic field modulation for detection purposes was employed and a Stanford SR830 lock-in amplifier converted the modulated signal to a DC voltage. The transmission EPR instrument employed no resonant cavity.

Results

X-ray crystallography revealed that nickel ions are hexa-coordinated by four oxygen atoms of the carboxylate and hydroxyl groups and by two imidazole nitrogen atoms, to form a distorted octahedral arrangement. The structure consists of a one-dimensional network of the complex molecules connected by strong intermolecular hydrogen bonds. Electronic bands (in the UV-vis-NIR electronic spectrum) were assigned to suitable spin-allowed transitions in the $D_{4h}$ symmetry environment. The single ion zero field splitting (ZFS) and $g$ parameters of the spin-triplet state of Ni(II) have been determined by high field and high frequency EPR spectroscopy giving $D = 5.77(1)$ cm$^{-1}$, $E = 1.636(2)$ cm$^{-1}$, $g_x = 2.29(1)$, $g_y = 2.18(1)$, $g_z = 2.13(1)$. These values allowed us to simulate the powder magnetic susceptibility and field-dependent magnetization of the complex.

Conclusions

The electronic spectroscopy data were successfully correlated with crystallographic and magnetic results. Assignment of the electronic bands to the respective transition in $D_{4h}$ symmetry, based on the Gaussian analysis, allowed the determination of the crystal field parameter, $Dq$, and of the Racah parameter, $B$. The ZFS parameters of the Ni(II) ions determined from the multiple frequency high-field EPR measurements were successfully applied to calculate the magnetic susceptibility and magnetization. This work adds substantial data to the characteristic of NiGlx1 models and is therefore relevant to the biochemistry of nickel.

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References