HIGH-FREQUENCY, HIGH-FIELD EPR, MAGNETIC SUSCEPTIBILITY AND X-RAY STUDIES ON A FERROMAGNETIC COMPLEX OF DIETHANOLAMINE (H₂L), [Cu₄(NH₃)₄(HL)₄][CdBr₄]Br₂·3dmf·H₂O


Introduction

In the recent literature there has been continuing interest in the magneto-structural studies on high-nuclearity transition-metal complexes with the studies aimed at the elucidation of the magnetic exchange interactions between paramagnetic metal ions, modeling structural and functional aspects of multimetallic active sites of biological metalloenzymes, and producing new nanometric materials such as molecular magnets. The magnetic properties of multicopper compounds have been extensively studied in the past, while successful EPR investigations have been much less frequent. In tetra-nuclear copper(II) compounds, the electronic spins of four copper (II) ions are coupled to give one quintet, three triplet, and two singlet spin states.

Experimental

The X-Ray structure of the title compound has been determined in this work¹. Magnetic susceptibility and magnetization measurements were performed by using a SQUID magnetometer. EPR spectra were taken at the 15/17 Tesla EMR facility of the NHMFL over the temperature range 3 – 300K, at frequencies 95, 190, 285 and 380 GHz.

Results and Discussion

The temperature dependence of the magnetic susceptibility was fitted to the spin Hamiltonian $H = J_{ab}S_aS_b + J_{bc}S_bS_c + J_{cd}S_cS_d + J_{ad}S_aS_d + J_{ac}S_aS_c$ with the exchange integrals $J_{ab} = J_{bc} = J_{cd} = -65(3)$ cm⁻¹ and $J_{ad} = J_{ac} = +1(3)$ cm⁻¹. Zero-field splitting was taken into account in the magnetic susceptibility calculations. High-Field EPR spectra due to the $S = 2$ ground state were fitted to the spin Hamiltonian

$H = \mu_B g \cdot B \cdot S + D \{S_z^2 - \frac{1}{3}S(S+1)\} + E \{S_x^2 - S_y^2\} + B_4^0O_4^0 + B_2^0O_2^2 + B_4^4O_4^4$

with $g_x = 2.138(1)$, $g_y = 2.142(1)$, $g_z = 2.067(1)$, $D = -0.3529(3)$ cm⁻¹, $E = -0.0469(8)$ cm⁻¹. The fourth-rank parameters $B_4^0$, $B_2^0$ and $B_4^4$ were found to be equal to zero within the error limits.

Conclusions

Ferromagnetic copper-copper exchange interactions are usually observed when the CuOCu angles are smaller than 97°. In the present compound, the very reduced overlap of the magnetic orbitals $x^2-y^2$ of interacting copper atoms that is caused by the specific geometric arrangement of the $[Cu_4(NH_3)_4(HL)_4][CdBr_4]Br_2·3dmf·H_2O$ cation results in the overall ferromagnetic interaction despite relatively large CuOCu angles of 107°. The magnetic dipole-dipole contribution to the D parameter was calculated equal to about 1/18 of D as determined from EPR, and carried opposite sign, indicating overwhelming contribution of the anisotropic exchange interactions to the zero-field splitting in the tetranuclear molecule.

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References