X-ray crystal structure and magnetic and photophysical properties of novel copper(II) *N*-oxide adduct $[(4\text{-MPyO})_2(CuCl_2)_2(H_2O)(C_2H_5OH)]$ (4-MPyO = 4-(4-methoxystyryl)pyridine *N*-oxide).

Autorzy

Yakov P. Nizhnik

Anna Szemik-Hojniak

Irena Deperasińska

Lucjan B. Jerzykiewicz

Maria Korabik

Marek Hojniak

V. P. Andreev

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A new mixed adduct, (4-MPyO)2(CuCl2)2(H2O)(C2H5OH) [where 4-MPyO is the 4-(4-methoxystyryl)pyridine N-oxide], was
obtained for the first time. It has been characterized by X-ray studies, IR, electronic absorption, and emission spectra,
lifetime measurements, and variable-temperature magnetic susceptibility measurements in the range 80–300 K. The
single-crystal X-ray diffraction shows that the geometry around both of the copper(II) ions can be described as a tetragonal
pyramid with a trapezoidal base at the corners of which are two oxygen atoms of N-oxide and two chlorine atoms. The
oxygen atoms of either water or ethanol are at the apex of the pyramid. Besides that, two molecules of the adduct form
a double-hydrogen-bonded superdimer in which they are connected to each other through hydrogen bonds of the
O-H · · · Cl type as formed between the chlorine atoms and ethanol molecule (Cl · · · O 3.22 Å). The copper(II) atoms
are antiferromagnetically coupled within a dimeric unit, and a singlet-triplet separation of 2J value (1100 cm-1) is greater
than the value expected from Hatfield's rule for the bridging angles Cu-O-Cu equal 108.9°and 110.2°. By means of
the PM3-calculated values of vertical excitation energies, the ligand-to-metal charge-transfer (LMCT) and the metal-toligand
charge-transfer transitions in the unresolved experimental absorption spectra of I have been revealed. From the
large Stokes shift value of emission spectra in solvents of different polarity (more than 6500 cm-1 in acetonitrile), the
charge-transfer (CT) nature of the emissive (LMCT) state of I has been concluded. Biexponential decay of the excited
complex in acetonitrile and frozen propanol suggests that the two different CT conformers (0.8, 4.12 ns and 1.99, 15.2
ns, respectively) are present in the excited state in solution while only one CT form is indicated by a monoexponential
decay (9.0 μs) in the solid.

Adres publiczny

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