Metal-Dependent Ferro- Versus Antiferromagnetic Interactions in Molecular Crystals of Square Planar {M(II) Imino-Nitroxide Radical} Complexes (M = Pt, Pd).

Fettouhi, Mohammed; El Ali, Bassam; Morsy, Mohammed; Golhen, Stephane; Ouahab, Lahcene; Le Guennic, Boris; Saillard, Jean-Yves; Daro, Nathalie; Sutter, Jean-Pascal; Amouyal, Edmond.
Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.
Inorganic Chemistry (2003), 42(4), 1316-1321.

Abstract

The synthesis and structural, spectral, and magnetic characterizations of two new complexes [Pt(IM2Py)Cl2] (A) and [Pd(IM2Py)Cl2] (B) are reported, where IM2Py is the imino-nitroxide radical ligand 2-(2-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl. Their crystal structures were solved at room temp. and at 120 K revealing structural phase transitions from pseudo-orthorhombic to monoclinic systems for the two compds. which remain isostructural in the whole temp. range explored. Structural parameters for A: T = 293 K [120 K], monoclinic (space group P21/n) [P21/c], a 7.906(2) [7.989(3)], b 17.872(9) [10.168(4)], c 10.357(3) [17.623(6)] .ANG., β 90.732(13)° [95.940(2)]°, Z = 4 [4]. Structural parameters for B: T = 293 K [120 K], monoclinic (space group P21/n) [P21/c], a 7.900(3) [7.9730(2)], b 17.907(9) [10.1806(3)], c 10.299(3) [17.7171(4)] .ANG., β 90.524(14)° [95.747(2)]°, Z = 4 [4]. In both complexes, the metal coordination is essentially planar. The av. Pt-N, Pt-Cl and Pd-N, Pd-Cl bond lengths are 1.996(6) [1.88], 2.295(2) [2.248(8)] .ANG. and 2.015(7) [2.029(8)], 2.287(3) [2.294(3)] .ANG., resp. The solid state structure was characterized by a pair-like mol. packing stacked in columns parallel to the a axis; this dimer character is reinforced at low temp. Despite their structural similarity, the study of the magnetic properties revealed that dominant ferromagnetic interactions govern the behavior of the Pt deriv. A, whereas antiferromagnetic interactions take place for the Pd compd. B. A rationalization for this rather intriguing difference is proposed in light of the spin population deduced from d. functional theory calcns. The electronic absorption spectra of A and B present structured absorption bands in the visible which are attributed to MLCT transitions. Both compds. are nonluminescent at room temp. However, a weak emission is detected for A in butyronitrile glasses at 77 K, indicating that the MLCT excited state is strongly quenched at low temp.