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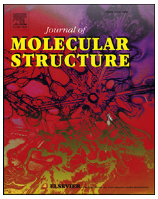

Synthesis, crystal structure, and π–π stacking magnetism of the mononuclear radical complex [N-hydrogenpyridinium][Pd(mnt)$_2$]

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ABSTRACT

The mononuclear radical anionic complex [N-hydrogenpyridinium][Pd(mnt)$_2$] (mnt = malonitrile-2,3-dithiolate) with a new countercation has been prepared and its crystal structure determined by X-ray crystallography. In the mononuclear radical anionic complex the palladium ion assumes a slightly distorted square-planar geometry and is bridged by four S atoms of two mnt anionic ligands. There are two kinds of slipped π–π stacking interactions between adjacent mononuclear radical anionic complexes in the crystal (i.e., PS-1 and PS-2). The ESR spectra, the variable-temperature susceptibilities, and the theoretical calculations reveal a very strong antiferromagnetic interaction between the adjacent mononuclear radical anionic complexes, leading to diamagnetism of the present complex. Further, the theoretical calculations indicate that the strong antiferromagnetic strength should be attributed to the PS-1 slipped π–π stacking interaction; the large spin densities on the associated short contact atoms should be a major factor leading to the strong magnetic coupling strength. This study is the first to reveal the mechanism of the strong antiferromagnetic interaction of a mononuclear radical anionic palladium complex with mnt as ligand.

1. Introduction

Palladium complexes have been of interest to chemical researchers for many years. Recently, for example, the intramolecular redox properties of some palladium complexes [1–3] have been shown to be useful in cooperative bond activation processes and catalysis. In addition, some palladium complexes have been shown to play an important role in molecular magnetism [4]. Of these, the mononuclear radical anionic palladium complexes with mnt as ligand [5–8] are of particular interest, since these complexes have been shown to display strong antiferromagnetic coupling strengths due to π–π stacking interactions. The published radical anionic complexes containing mnt as ligand have revealed that the countercations affect the intermolecular interactions of the coordinated radical anions; namely, different π–π stacking models can be obtained with different countercations. However, in the palladium radical anionic complexes with mnt as ligand, the factors that result in the strong antiferromagnetic coupling interactions have not been revealed to date. In order to understand the factors that dominate the strong antiferromagnetic coupling interaction of the palladium radical anionic complexes with mnt as ligand and to further understand the correlation between spin density and π–π stacking magnetic coupling strength, we synthesized the present mononuclear radical anionic complex. Herein, we report its synthesis, crystal structure and π–π stacking magnetic coupling mechanism, including the correlation between its magnetic coupling strength and spin densities on associated short contact atoms.

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2. Experimental

2.1. Materials

N-hydrogenpyridinium bromide [9] was prepared according to the literature. All other chemicals were analytical grade and used without further purification.

2.2. Preparation of complex [N-hydrogenpyridinium]$_2$[Pd(mnt)$_2$]

A mixture containing 5 mL water and $PdCl_2$ (0.4800 g, 2.71 mmol) was added into a 10 mL methanol solution of Na_2mnt (1.8600 g, 9.99 mmol). This mixture was stirred and refluxed for one hour, and then a 20 mL water solution of N-hydrogenpyridinium bromide (3.3200 g, 20.70 mmol) was added into the refluxed reactants in drops, over which time a sediment appeared. Deep orange microcrystals were obtained after recrystallization of the sediment from diethyl ether (yield: 78%, based on $PdCl_2$). IR (cm^{-1}): 3060(s), 3030(s), 1990(w), 1940(w), 1870(w), 1450(s), 1150(s), 1070(s), 764(s). Elemental anal. Calcd for $C_{18}H_{12}N_6PdS_4$ (FW 547.008): C: 39.52%; H, 2.21%; N, 15.36%; Pd, 19.45%. Found: C, 39.80; H, 2.53; N, 15.01; Pd, 19.93%. ^{13}C NMR (600 MHz, DMSO − d_6) δ (ppm): 155.3, 139.5, 125.9.

2.3. Preparation of complex [N-hydrogenpyridinium][Pd(mnt)$_2$]

A 5 mL acetone solution of iodine (0.1270 g, 0.50 mmol) was added into a mixed solution of acetone (5 mL) and ethanol (30 mL) containing [N-hydrogenpyridinium]$_2$[Pd(mnt)$_2$] (0.5000 g, 0.91 mmol), and the mixed solution was stirred for ten minutes and then filtered. Black single crystals were obtained after the filtrate was allowed to stand and slowly evaporate at room temperature for one week (yield: 18%, based on [N-hydrogenpyridinium]$_2$[Pd(mnt)$_2$]). IR (cm^{-1}): 2108(s), 1629(m), 1480(s), 1452(s), 1154(s), 757(s), 674(vs), 495(s). Elemental anal. Calcd for $C_{13}H_6N_5PdS_4$ (FW 466.87): C, 33.44; H, 1.30; N, 15.00; Pd, 22.79%. Found: C, 33.16; H, 1.62; N, 15.31; Pd, 22.40%.

2.4. Physical measurements

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm^{-1} region following KBr disk sample preparation. C, H and N elemental analyses were carried out on a Perkin–Elmer 2400 instrument, and Pd content was measured on an inductively coupled plasma atomic emission spectrometer model IRIS Intrepid II. ^{13}C NMR spectrum was performed on a Varian AS600 equipment. At 25 °C, X-band ESR spectra in solid and acetonitrile solution (0.002 mol/dm^3) were recorded on an electron spin resonance spectrometer model Bruker A300. Variable-temperature magnetic susceptibilities of a microcrystalline powder sample were measured in a magnetic field of 1 kOe in the temperature range 5.00–300 K on a SQUID magnetometer. The data were corrected for the magnetization of the sample holder and for the diamagnetic contributions of the complexes, which were estimated from Pascal's constants.

2.5. X-ray crystallography

A black single crystal with dimensions of 0.30 × 0.25 × 0.10 mm was selected and glued to the tip of a glass fiber. The crystal structure determination was carried out at 25 °C on an X-ray diffractometer (Bruker Smart-1000 CCD) using a graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) in the range of $3.76 < 2\theta < 54.00°$. A total of 9328 reflections were collected, of which 3520 were independent ($R_{int} = 0.039$), and 2869 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. Corrections for *Lp* factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in the calculated positions and refined as riding. The programs for structure solution and refinement were SHELXS-97 and SHELXTL-97. The pertinent crystallographic data and structural refinement parameters are summarized in Table 1.

2.6. Computational details

All the calculations are based on the relevant π–π stacking models (Figs. 5 and 6), in which the bond length data, the associated angles, and the relevant locations of the adjacent π–π stacking complexes were taken from the X-ray structures of the relevant crystal.

The magnetic coupling constants and spin densities of the models were studied using density functional theory (DFT) with the broken-symmetry approach (BS) [10–12]. The exchange coupling constants *J* were evaluated by calculating the energy difference between the high-spin state (E_{HS}) and the broken symmetry state (E_{BS}). Assuming the spin Hamiltonian is defined as

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \tag{1}$$

with $\hat{S}_1 = \hat{S}_2 = \frac{1}{2}$ the *J* value for the π–π stacking between two radical anionic palladium complexes was obtained from Equation (2), which was proposed by Noodleman [10–12]:

$$J = \frac{E_{BS} - E_{HS}}{S_{Max}^2} \tag{2}$$

in which S_{Max} is 1. To obtain exchange coupling constants *J*, Orca 2.8.0 calculations [13] were performed with the B3LYP level of theory as proposed by Becke [14,15] and Lee et al. [16], which can provide *J* values in agreement with the experimental data for transition metal complexes. The def2-TZVP basis set [17,18] as proposed by Ahlrichs and co-workers was used for all atoms in our calculations. Strong convergence criteria was used in order to ensure that the results are well converged with respect to technical parameters (the system energy was set to be smaller than 10^{-7} hartree).

Table 1
Crystallographic data of the title complex.

Formula	$C_{13}H_6N_5PdS_4$
Mr	466.87
T(K)	298 (2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	6.774 (4)
b(Å)	17.051 (9)
c(Å)	14.305 (8)
β(°)	101.628 (8)
V (Å^3)	1618.4 (15)
Z	4
D_c(g·cm^{-1})	1.916
μ(mm^{-1})	1.666
Reflections collected	9328
Unique reflections/R_{in}	3520/0.0394
$R_1[I > 2\sigma(I)]$	0.0407
wR_2 (all data)	0.0898
GOF	1.048
$(\Delta\rho)_{Max}$ (eÅ^{-3})	0.808
$(\Delta\rho)_{Min}$ (eÅ^{-3})	−0.531