# A strong antiferromagnetic interaction between imino nitroxides through a Pd$^{II}$ ion

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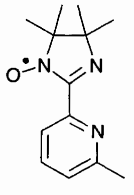
**A palladium(II) complex with imino nitroxides, [PdCl$_2$(immepy)$_2$] [immepy = 2-(6-methylpyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy], shows a strong antiferromagnetic interaction between the coordinated imino nitroxides, which results from indirect overlap of radical SOMOs through a $d_{xy}$ orbital.**

Typically, magnetic interactions between paramagnetic centres through diamagnetic metal ions are negligibly small or weakly antiferromagnetic. Recently, some metal complexes with organic radical ligands, in which the metal ions are diamagnetic, have been proven to mediate substantial magnetic interactions. For example, metal complexes with semiquinones show a variety of magnetic interactions depending on metal ions and coordination geometries, and the magnitude of the magnetic interactions through diamagnetic ions depend strongly on the energy of $d_\pi$ orbitals. A series of square-planar metal complexes [M$^{II}$(sq)$_2$] (M = Ni, Pd, Pt; sq = *tert*-butyl-substituted semiquinone) showed fairly strong antiferromagnetic interactions due to indirect overlap of the magnetic orbitals through the metal $d_\pi$ orbitals and the strength of inter-radical exchange increases down to the series of metal ions.[1] [M$^{III}$(3,6-dbsq)$_3$][2] (M = Al, Ga; 3,6-dbsq = 3,6-di-*tert*-butylsemiquinone) and [Ga$^{III}$(3,5-dtbsq)$_3$] (3,5-dtbsq = 3,5-di-*tert*-butyl-1,2-benzosemiquinone)[3] showed weak ferromagnetic interactions ($J$ = 6.2, 8.6, 7.8 cm$^{-1}$, respectively, where $H = -2JS_i \cdot S_j$), and [M$^{IV}$(cat-N-SQ)$_2$] (M = Ti, Ge, Sn; cat-N-SQ = tridentate Schiff-base biquinone)[4] were characterized by a triplet ground state with exchange coupling constants of $J = -56, -27, -23$ cm$^{-1}$ ($H = JS_1 \cdot S_2$), respectively. The ferromagnetic interactions observed were understood by orthogonal coordination of the semiquinones. On the other hand, metal complexes with nitronyl nitroxides or imino nitroxides have been extensively studied, and some of them have shown a magnetic ordering at low temperature.[5] Copper(I) imino nitroxide, [Cu$^I$(immepy)$_2$]PF$_6$ [immepy = 2-(6-methylpyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy] showed a ferromagnetic interaction ($2J$ = 103 cm$^{-1}$) through the diamagnetic Cu$^I$ ion.[6] However, magnetic interactions of imino nitroxides or nitronyl nitoxides through diamagnetic metal ions are not well understood. We report here the synthesis, structure, and magnetic properties of a palladium(II) complex with imino nitroxides, [PdCl$_2$(immepy)$_2$] **1**.

Complex **1** was prepared by reacting 55 mg (0.2 mmol) of [NH$_4$]$_2$[PdCl$_4$] dissolved in 15 ml of methanol with 90 mg (0.4 mmol) of immepy.[7] After standing overnight, dark red crystals precipitated and one of them was subjected to X-ray analysis.†‡



immepy

The complex molecule has a centre of symmetry at the Pd$^{II}$ ion (Fig. 1). The square-planar coordination sites at Pd$^{II}$ are occupied by two chlorine and two N atoms from the immepy ligands with a *trans* arrangement, where immepy acts as a monodentate ligand. The Pd–Cl and Pd–N(1) bond lengths are 2.2977(7) and 2.019(2) Å, respectively, and the Cl–Pd–N(1) bond angle is 87.72(5)°. The imino nitroxyl plane [N(1)C(7)N(2)O(1)] tilts 94.0(2)° with respect to the square-planar coordination plane of Pd$^{II}$. The magnetic susceptibility data of **1** are shown in the form of a $\chi_m T$ *vs.* $T$ plot,§ where $\chi_m$ is the molar magnetic susceptibility (Fig. 2). The $\chi_m T$ value shows a substantial decrease as the temperature decreases, reaching a plateau (0.040 emu mol$^{-1}$ K) at 25 K, where the non-zero $\chi_m T$ value is due to a paramagnetic impurity. The observed magnetic behaviour is quite characteristic of an antiferromagnetically coupled biradical. The magnetic data permit determination of the triplet–singlet energy gap ($2J$). The least-squares fitting for the data by the Bleaney–Bowers equation ($H = -2JS_1 \cdot S_2$)[8] gives the best fit parameters $2J$ and $g$ values of $-168.0(4)$ cm$^{-1}$ and 2.00(1), respectively, assuming a 0.07(4) mole fraction of paramagnetic impurity. EPR spectra§ of a powdered sample at 293 and 77 K and a frozen ethanol solution at 77 K were measured and did not show any significant feature other than a weak feature at 0.33 T attributable to a radical impurity. The absence of an EPR signal for the frozen ethanol solution indicates that the observed antiferromagnetic interaction is not intermolecular but intramolecular in nature. The UV–VIS absorption spectra of **1** as well as that of immepy and [NH$_4$]$_2$[PdCl$_4$] are shown in Fig. 3.§ In methanol solution,

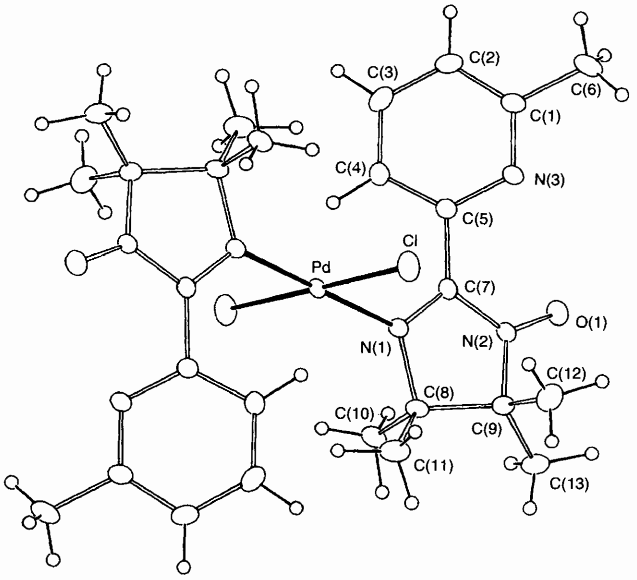


**Fig. 1** ORTEP diagram of **1** with 50% probability ellipsoids. Selected bond distances (Å) and angles (°): Pd–Cl 2.2977(7), Pd–N(1) 2.019(2), O(1)–N(2) 1.264(3), N(1)–C(7) 1.297(3), N(2)–C(7) 1.386(3), Cl–Pd–N(1) 87.72(5), Pd–N(1)–C(7) 125.9(1), Pd–N(1)–C(8) 124.3(1), C(7)–N(1)–C(8) 109.3(2), O(1)–N(2)–C(7) 126.5(2), N(1)–C(7)–N(2) 111.3(2).

**1** shows absorption bands at 350 nm ($\varepsilon$ = 7800 dm$^3$ mol$^{-1}$ cm$^{-1}$) and 500 (1800), which were not observed in the UV–VIS spectra of the starting materials. An electronic spectrum of [$PdCl_2$(bpy)] has been studied,[9] this exhibited an absorption band at 317 nm which was assigned to an MLCT band. A molecular-orbital calculation of the immepy ligand showed that the singly occupied molecular orbital (SOMO) is centred mainly on the imino nitroxide fragment, while the next lowest unoccupied orbital (NLUMO) is delocalized over the whole $\pi$ system.[10] Therefore, the absorption bands at 350 and 500 nm in **1** would correspond to metal-to-NLUMO and metal-to-SOMO transitions, respectively. As shown in the structural analysis, the coordination plane of the Pd$^{II}$ ion is perpendicular to the imino nitroxyl plane, where the SOMO ($p_{\pi^*}$ orbital) is perpendicular to the imino nitroxyl plane. This implies that the metal $d_{xy}$ orbital has a substantial overlap with the SOMOs, facilitating MLCT interaction, leading to the strong antiferromagnetic interaction between the imino nitroxides.

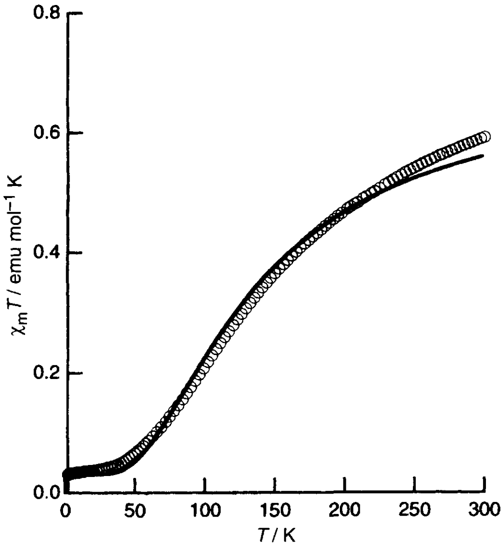


**Fig. 2** $\chi_m T$ *vs.* $T$ plot of **1**. The solid line corresponds to the best fit curve by using the parameters given in the text.

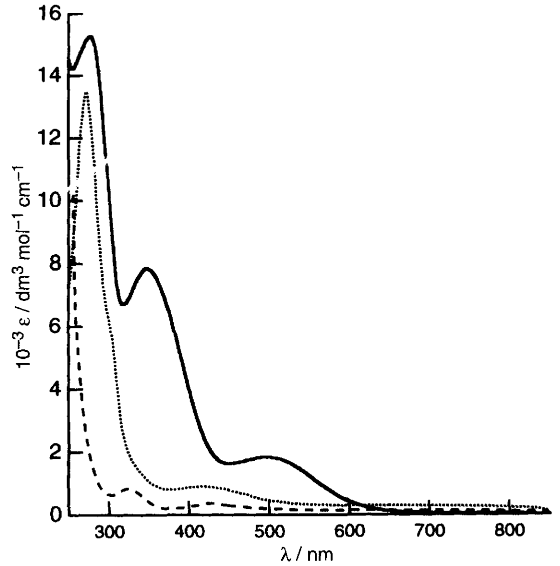


**Fig. 3** UV-VIS spectra of (—) **1**, (···) immepy and (---) [$NH_4$]$_2$[$PdCl_4$]

## Footnotes

† Elemental analysis for **1**: Found: C, 48.2; H, 5.8; N, 12.7. Calc. for [$PdCl_2$(immepy)$_2$]: C, 48.7; H, 5.7; N, 13.1%.

‡ *Crystal data for* $C_{26}H_{36}Cl_2N_6O_2Pd$ **1**: $M$ = 641.94, monoclinic, space group $P2_1/n$, $a$ = 10.396(2), $b$ = 12.736(2), $c$ = 11.219(2) Å, $\beta$ = 103.86(1)°, $U$ = 1442.2(4) Å$^3$, $Z$ = 2, $D_c$ = 1.478 g cm$^{-3}$, $T$ = 293 K, dark red tablet, 0.2 × 0.2 × 0.3 mm, $\mu$ = 8.63 cm$^{-1}$. A single crystal of **1** was mounted on a glass fibre with epoxy resin. Diffraction data were collected on Rigaku 7S four-circle diffractometer equipped with graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.710 69 Å). Three standard reflections were measured every 200 data collections, and revealed no fluctuation in intensities. The lattice constants were optimized from a least-squares refinement of the settings of 25 carefully centred Bragg reflections in the range $25 < 2\theta < 30°$. All data were corrected for Lorentz and polarization effects and empirical absorption corrections ($\psi$ scans) were carried out. The minimum and maximum transmission factors were 0.957 and 1.000. The structure was solved by direct methods with SHELX-86 (G. M. Sheldrick, University of Göttingen, 1986) and Fourier techniques, and refined by full-matrix least squares using XTAL 3.2 (S. R. Hall and J. M. Stewart, Universities of Western Australia and Maryland, 1992). All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. Hydrogen atoms were included in the refinement with isotropic thermal parameters. The refinement of 241 parameters converged to $R$ = 0.025 and $R_w$ = 0.032 [for 2722 reflections with $I_0 > 3\sigma(I_0)$].

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/107.

§ Variable-temperature magnetic susceptibility measurements on **1** in the region 2–300 K using a 10000 G field were made using a SQUID magnetometer (Quantum Design) with a sample sealed in a gelatine capsule. Diamagnetic correction for the sample holder was applied to the data. Diamagnetic correction for the sample was determined from Pascal's constants and literature values. UV-VIS spectra for methanol solutions were recorded on a Hitachi UV-340 spectrometer. EPR spectra were recorded on a JEOL FE2XG spectrometer operating at X-band frequency with a magnetic field modulation of 100 kHz.

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