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Intramolecular exchange interaction in twofold spin-labelled platinum complexes

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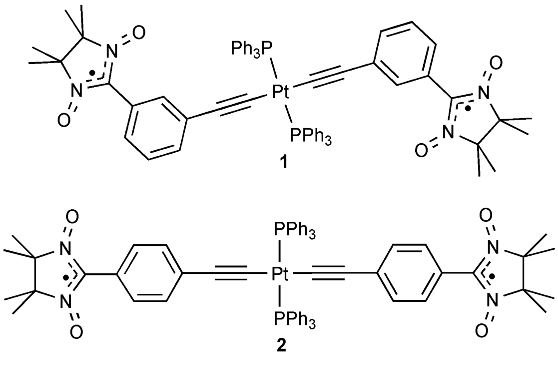
Received (in Cambridge, UK) 10th May 2004, Accepted 13th July 2004
First published as an Advance Article on the web 6th August 2004

The synthesis and the crystal structures of two platinum bis-ethynyl-phenyl-nitronyl-nitroxide complexes are reported and solution EPR investigations evidenced the intramolecular exchange interaction through a diamagnetic transition metal based spacer.

Platinum complexes are very attractive molecules for their electronic[1] and photophysical[2] properties. However, few spin-labelled platinum complexes have been reported in the literature[3] and mostly pyridine-nitronyl-nitroxide coordinating ligands have been used.[4] Even if the presence of an intramolecular magnetic interaction in such diradicals has been shown by solution EPR spectroscopy,[5] precise information about the exchange interaction through a diamagnetic platinum metal is lacking. To gain better insight into the mechanisms governing the intramolecular communication in such systems with diamagnetic transition metal ions, we synthesized and investigated two diradicals based on organometallic *trans*-platinum(II) complexes of ethynyl-phenyl-nitronyl-nitroxides (Scheme 1). In this communication, we present the synthesis of the two new terminal spin-labelled molecular rods **1** and **2** and their characterization by several techniques.† X-ray crystal structures of the diradicals are described and the EPR spectra of the fluid and frozen diluted solutions are discussed.

The diradicals **1**‡ and **2**§ have been prepared by reacting two equivalents of the corresponding *meta*- or *para*-ethynyl-phenyl-nitronyl-nitroxide radicals with *trans*-bis-(triphenylphosphine)-dichloro-platinum in the presence of CuI in a mixture of THF–iPr$_2$NH 10 : 1. The pure products could be obtained by chromatography on SiO$_2$ in 72% and 97% yield for **1** and **2** respectively and single crystals were grown from a THF–MeCN solution for **1** and CH$_2$Cl$_2$–hexane for **2**.¶ The starting radicals were obtained by an adapted synthesis.[6]

The MALDI-TOF spectra of both complexes show the fragmentations corresponding to the successive loss of four oxygen atoms, a pattern typical of nitronyl-nitroxide diradicals.[7] The characteristic ν_{NO} vibration band (1360 cm^{-1} for **1** and 1362 cm^{-1} for **2**) together with the $\nu_{\mathrm{C\equiv C}}$ (2107 cm^{-1} for **1**, 2114 cm^{-1} for **2**) can be seen on the IR spectra. The UV-visible spectra show the absorption band corresponding to the n → π* (605 nm, ε = 1250 M^{-1} cm^{-1} for **1**, 645 nm, ε = 1180 M^{-1} cm^{-1} for **2**) of the blue nitronyl-nitroxide with an extinction coefficient ε in agreement with a diradical.



Scheme 1

X-ray crystal structures have been obtained for both radicals. Figures 1 and 2 show the ORTEP views of the two corresponding molecules, the first one containing two THF solvate molecules in the unit cell. The nitronyl-nitroxides have bond lengths characteristic of such radicals having an unpaired electron equally shared between two equivalent NO groups (NO = 1.28–1.30 Å, CN = 1.34–1.35 Å).[8] The dihedral angle formed by the mean planes of the radicals and the adjacent phenyl is also typical of nitronyl-nitroxides (29.4° for **1**, 27.5° for **2**). Interestingly, the aromatic rings are twisted from the Pt–P bond by *ca.* 35.8° for **1** and 30.4° for **2**. The Pt–C (2.00–2.01 Å) and C≡C (1.20–1.17 Å) bond lengths are in the expected range for such complexes.

The room temperature EPR spectra of *ca.* 10^{-4} M CH$_2$Cl$_2$ degassed solution of **1** and **2** exhibit a nine line pattern centred at $g \cong 2.0066$ ($a_{\mathrm{N}} \cong 3.7$ G) for **1** and centred at $g \cong 2.0094$ ($a_{\mathrm{N}} \cong 3.7$ G) for **2** (Figs. 3 and 4). Such features are characteristic of a bis-nitronyl-nitroxide where the unpaired spins of the terminal radical fragments are in exchange ($|J| \gg a_{\mathrm{N}}$ in energy units) for each complex. The apparent *g*-shift observed for **2** may result from spin-orbit coupling through the molecular orbital overlap of the π-radical with d-orbitals of the Pt ion. These features are consistent with an electronic communication within the platinum based spacer. Even if communication over large distances has been reported,[9] the rigid structure of the molecules supports an exchange interaction through the diamagnetic transition metal atom. The hyperfine coupling to the ^{195}Pt nucleus or to ^{31}P is not observed.

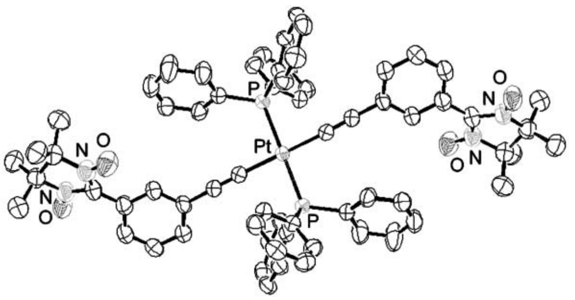


Fig. 1 ORTEP drawing of **1**.

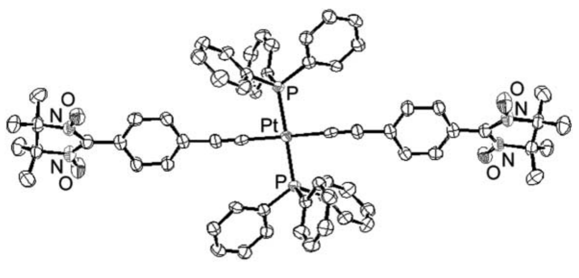


Fig. 2 ORTEP drawing of **2**.

DOI: 10.1039/b407067d

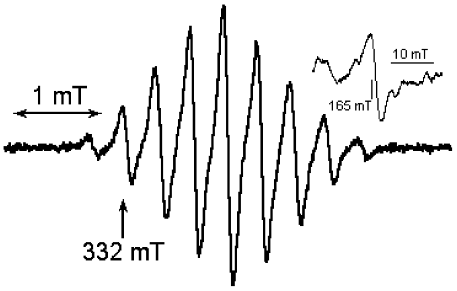


Fig. 3 EPR spectrum of **1** in fluid solution. Inset: $\Delta M_S = \pm 2$ of the powder at 4 K.

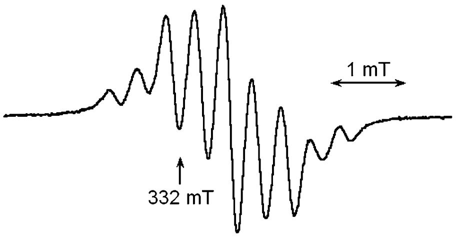


Fig. 4 EPR spectrum of **2** in fluid solution.

Frozen CH_2Cl_2 diluted solution at 4 K showed a "half-field" $\Delta M_S = \pm 2$ resonance, associated with the existence of a triplet state, for compound **1**. Interestingly, such a pattern could not be observed for compound **2**, presumably due to a slightly larger inter-spin distance in this compound. The temperature dependence of the integrated intensity of the $\Delta M_S = \pm 1$ line shows a pure Curie law within experimental error.

As a consequence of the shape of the spectra in fluid solution featuring the limit of strong exchange interaction, *i.e.* $|J| \gg a_N$, a lower limit of the exchange interaction would correspond to *ca.* 0.1 cm^{-1} for a few hundreds of hyperfine splitting. The absence of significant departure of the I.T = f(T) curve from a constant behaviour at low temperature may be qualitatively used for the estimation of the higher limit of $|J|$. Assuming a singlet–triplet equilibrium for this two-spin system, a simulation shows no deviation of the I.T = f(T) curve within 10% variation around the high temperature limit down to 4 K when $|J| \leqslant 1$ cm^{-1}.

In conclusion, despite the weak spin density located on the triple bond carbon atoms of ethynyl-phenyl-nitronyl-nitroxide radicals, an electronic communication takes place in these two new complexes. In view of the molecular structure of both compounds, a reasonable pathway for this exchange interaction involves the d orbitals of the square planar d^8 platinum metal.

The synthesis of *cis*-platinum complexes is currently under investigation and further studies to gain better insight into the intramolecular exchange interaction will be performed.

We thank the Networkproject MOLMEM, German Ministry of Education and Research (BMBF-FZK 13 N 8360) for financial support and the Alexander von Humboldt Foundation for a post-doctoral fellowship to C. S.

Notes and references

† Synthesis of **1** and **2**: *trans*-$PtCl_2(PPh_3)_2$ (80 mg scale), ethynyl-(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-yloxyl)-phenyl (*ca.* 2 equiv.) and CuI (*ca.* 10 mol%) in THF (10 ml) and $i Pr_2NH$ (1 ml) are stirred at rt under Ar during 1 to 2 h. The solvent is evaporated or the reaction mixture is filtered through a short column packed with SiO_2 (elution: THF) before evaporation. The pure metallic-blue products are obtained by chromatography on SiO_2 (CH_2Cl_2–MeCN).

‡ SiO_2 (CH_2Cl_2–MeCN 9 : 1). Yield: 72%. MALDI-TOF (1,8,9-anthracenetriol): 1232.7 $[M]^+$, 1216.7 $[M - O]^+$, 1201.7 $[M - 2O + H]^+$, 1185.7 $[M - 3O + H]^+$, 1169.7 $[M - 4O + H]^+$. IR (KBr pellets): 3438, 3056, 2989, 2107 ($\nu_{C\equiv C}$), 1590, 1572, 1481, 1435, 1417, 1387, 1360 (ν_{NO}), 1305, 1218, 1166, 1140, 1098, 794, 746, 708, 691, 540, 521, 456. UV-vis (CH_2Cl_2) λ, nm (ε, M^{-1} cm^{-1}): 605 (1250), 350 (53840), 268 (69510), 226 (95560). R_f (SiO_2, CH_2Cl_2–MeCN 9 : 1): 0.42. EPR (CH_2Cl_2, rt): 9 lines, $a_N = 3.7$ G, $g = 2.0066$. Anal. calcd for $C_{66}H_{62}N_4O_4P_2Pt$ ($M_r = 1232.25$): C, 64.33; H, 5.07; N, 4.55. Found: C, 64.28; H, 4.82; N, 4.23%. Mp: 207–209 °C (dec).

§ SiO_2 (CH_2Cl_2–MeCN 97 : 3). Yield: 97%. MALDI-TOF (1,8,9-anthracenetriol): 1217.2 $[M - O + H]^+$, 1201.2 $[M - 2O + H]^+$, 1186.2 $[M - 3O + 2H]^+$, 1170.2 $[M - 4O + 2H]^+$. IR (KBr pellets): 3443, 3055, 2982, 2937, 2114 ($\nu_{C\equiv C}$), 1598, 1480, 1435, 1418, 1385, 1362 (ν_{NO}), 1300, 1219, 1184, 1166, 1132, 1098, 837, 743, 707, 689, 512. UV-vis (CH_2Cl_2) λ, nm (ε, M^{-1} cm^{-1}): 645 (1180), 372 (71350), 308 (31760), 225 (77310). R_f (SiO_2, CH_2Cl_2–MeCN 94 : 6): 0.25. EPR (CH_2Cl_2, rt): 9 lines, $a_N = 3.7$ G, $g = 2.0094$. Anal. calcd for $C_{66}H_{62}N_4O_4P_2Pt$ ($M_r = 1232.25$): C, 64.33; H, 5.07; N, 4.55. Found: C, 64.61; H, 4.81; N, 4.24%. Mp: 212–215 °C (dec).

¶ *Crystal data and structure refinement for* **1** *and* **2**: Data were collected at 200 K on a STOE diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares analysis. **1**, $M = 1376.43$, triclinic, space group $P\bar{1}$, with $a = 9.752(2)$, $b = 12.068(2)$, $c = 14.920(3)$ Å, $\alpha = 76.54(3)$, $\beta = 89.08(3)$, $\gamma = 69.46(3)^\circ$, $V = 1595.0(6)$ Å^3, $Z = 1$, $D_c = 1.433$ Mg m^{-3}, $\mu = 2.307$ mm^{-1}. 369 parameters were refined using 5796 unique observed reflections $[I > 1\sigma(I)]$ to give R (all data) = 0.0476 and $wR2$ (all data) = 0.1217. **2**, $M = 1232.23$, monoclinic, space group $C2/c$, with $a = 34.963(7)$, $b = 9.4928(19)$, $c = 19.323(4)$ Å, $\beta = 119.33(3)^\circ$, $V = 5591.3(19)$ Å^3, $Z = 4$, $D_c = 1.464$ Mg m^{-3}, $\mu = 2.620$ mm^{-1}. 349 parameters were refined using 3530 unique observed reflections $[I > 1\sigma(I)]$ to give R (all data) = 0.0452 and $wR2$ (all data) = 0.1018. CCDC 238541 and 238542. See http://www.rsc.org/suppdata/cc/b4/b407067d/ for crystallographic data in .cif or other electronic format.

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