# Receptors for the Hydrazinium Ion. Simultaneous First- and Second-sphere Coordination inside Organopalladium Crown Ether Complexes

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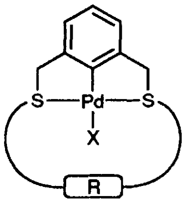
Organopalladium crown ether complexes are employed to bind the hydrazinium ion, $[NH_2NH_3]^+$, *via* simultaneous first- and second-sphere coordination featuring σ-donation to Pd and hydrogen bonding to aliphatic ether oxygen atoms.

Second-sphere coordination can be modelled by the interaction of crown ethers with coordinated ligands such as ammonia in which the metal-bound $NH_3$ group hydrogen bonds to the crown ether oxygen atoms, reminiscent of an ammonium cation.[1] In a few instances, complexes have been characterized that involve simultaneous first- and second-sphere coordination,[1,2] but it is only recently that this type of multiple-point binding has been accomplished by design and used to bind interesting substrates such as barbiturates[3] and amino acids.[4] In this regard, we recently reported the synthesis and binding properties of a series of macrocyclic organopalladium complexes (Scheme 1), which exhibit molecular recognition properties for DNA nucleobases employing simultaneous first- and second-sphere coordination.[5]

Coordination of the hydrazine molecule to a transition metal complex has been suggested as an intermediate in the



$L^1$: R = $(CH_2)_{11}$
$L^2$: R = $(CH_2)_2O(CH_2)_2$
$L^3$: R = $(CH_2)_2O[(CH_2)_2O]_2(CH_2)_2$
$L^4$: R = $(CH_2)_2O[(CH_2)_2O]_4(CH_2)_2$
$L^5$: R = *p*-$CH_2(C_6H_4)O[(CH_2)_2O]_3(C_6H_4)CH_2$
$L^6$: R = *m*-$CH_2(C_6H_4)O[(CH_2)_2O]_3(C_6H_4)CH_2$

**Scheme 1**

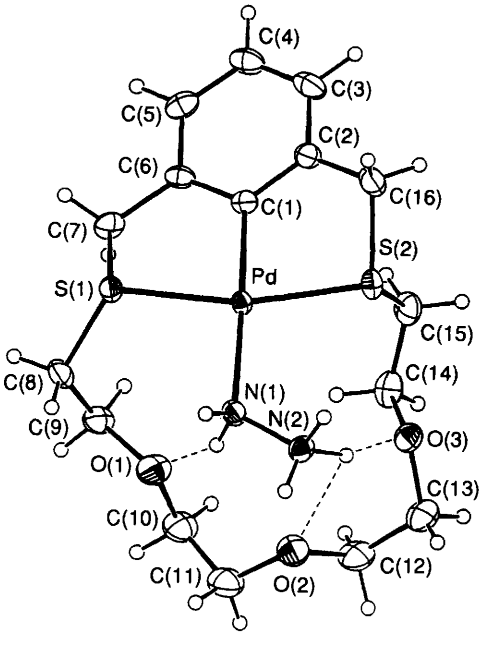


**Fig. 1** ORTEP drawing of the $[Pd(L^3)(NH_2NH_3)]^{2+}$ cation showing the atom numbering scheme. Significant bonding parameters are Pd–S(1) 2.289(2), Pd–S(2) 2.313(3), Pd–N(1) 2.166(6), Pd–C(1) 1.984(6), N(1)–N(2) 1.440(8) Å; S(1)–Pd–S(2) 165.98(7), N(1)–Pd–C(1) 177.5(2), S(1)–Pd–N(1) 94.6(2), S(2)–Pd–N(1) 98.5(2), S(1)–Pd–C(1) 83.1(2), S(2)–Pd–C(1) 83.8(2)°; N(1)···O(1) 2.885(8), N(2)···O(2) 2.956(9), N(2)···O(3) 2.952(8) Å.

metal-mediated reduction of dinitrogen to ammonia[6] and the direct catalytic reduction of metal-bound hydrazine to ammonia in acidic media has been reported.[7] Herein, we report that the receptors $[Pd(L^3)(MeCN)]^+$ and $[Pd(L^4)(MeCN)]^+$, containing three and five ether oxygens, respectively, act as excellent receptors for the protonated form of hydrazine, the hydrazinium ion, $[NH_2NH_3]^+$, utilizing simultaneous first- and second-sphere coordination and involving as many as seven interactions between receptor and substrate.

The metal-free macrocycles, $L^3$ and $L^4$, were prepared in dimethylformamide (DMF) by the $Cs^+$-mediated ring-closure reaction of *m*-xylene-α,α′-dithiol with the appropriate ditosylate in 80–90% yield.[8] The palladium and labile MeCN group were introduced through direct metallation of the aromatic ring using $[Pd(MeCN)_4][BF_4]_2$ in MeCN,[9] resulting in yields of receptor of 86 and 77% for $[Pd(L^3)(MeCN)]^+$ and $[Pd(L^4)(MeCN)]^+$, respectively.† The reaction of hydrazinium monochloride, $[NH_2NH_3]Cl$, with $AgBF_4$ (1 equiv.) in MeCN results in the formation of $[NH_2NH_3][BF_4]$, which, upon the addition of 1 equiv. of metalloreceptor gave immediate quantitative formation of $[Pd(L^3)(NH_2NH_3)]^{2+}$ and $[Pd(L^4)(NH_2NH_3)]^{2+}$. The $^1H$ NMR spectra of these two complexes in acetone solution demonstrate that the hydrazinium ion is bound to palladium but the fluxional nature of the hydrogen bonding did not allow the exact nature of the receptor/substrate interactions in solution to be determined. However, the X-ray structure determination[10] for both compounds‡ show unambiguously the extent of the metallo-

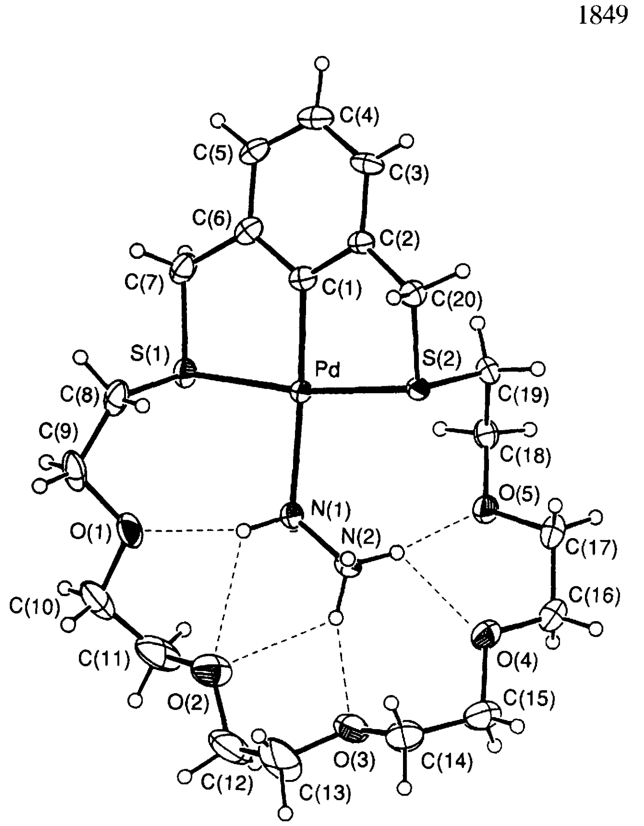


**Fig. 2** ORTEP drawing of the $[Pd(L^4)(NH_2NH_3)]^{2+}$ cation showing the atom numbering scheme. Significant bonding parameters are Pd–S(1) 2.306(2), Pd–S(2) 2.313(2), Pd–N(1) 2.170(6), Pd–C(1) 1.972(7), N(1)–N(2) 1.431(8) Å; S(1)–Pd–S(2) 170.76(7), N(1)–Pd–C(1) 176.6(3), S(1)–Pd–N(1) 91.2(2), S(2)–Pd–N(1) 98.1(2), S(1)–Pd–C(1) 85.5(2), S(2)–Pd–C(1) 85.3(2)°; N(1)···O(1) 2.853(7), N(1)···O(2) 3.005(8), N(2)···O(2) 3.053(8), N(2)···O(3) 2.834(8), N(2)···O(4) 2.782(7), N(2)···O(5) 2.773(8) Å.

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† $^1H$ NMR (300 K, $CDCl_3$): $[Pd(L^3)(MeCN)][CF_3SO_3]_2$ δ 6.99–7.08 (m, 3H), 4.56 (s, 4H), 4.21 (s, 4H), 3.71 (s, 4H), 3.65 (s, 4H), 3.36 (t, 4H), 2.21 (s, 3H); $[Pd(L^4)(MeCN)][BF_4]_2$ δ 6.88–6.99 (m, 3H), 4.36 (s, br, 4H), 3.96 (s, 4H), 3.60–3.70 (m, 16H), 3.32 (s, 4H), 2.07 (s, 3H). $^1H$ NMR [300 K, $(CD_3)_2CO$]: $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$ δ 7.00 (m, br, 3H), 4.50 (s, 4H), 4.15 (s, 4H), 3.72 (s, 4H), 3.67 (s, 4H), 3.40 (t, 4H), 2.44 (s, 5H); $[PC(L^4)(NH_2NH_3)][BF_4]_2$ δ 7.00 (m, 3H), 4.57 (s, br, 4H), 3.31–3.95 (m, br, 29H).

‡ *Crystal data* for $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$: *M* = 765.10, monoclinic $P2_1/c$, *a* = 11.906(4), *b* = 17.192(4), *c* = 15.313(4) Å, β = 111.18(2)°, *U* = 2923(4) Å$^3$, *Z* = 4, $D_c$ = 1.738 g cm$^{-3}$, μ(Mo-Kα) = 9.832 cm$^{-1}$. Rigaku AFC6S diffractometer, 2958 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, *R* = 4.07, $R_w$ = 4.39%.

For $[Pd(L^4)(NH_2NH_3)][BF_4]_2$: *M* = 728.67, triclinic $P\bar{1}$, *a* = 9.391(3), *b* = 18.292(5), *c* = 9.107(3) Å, α = 94.46(3)°, β = 102.02(3)°, γ = 103.52(2)°, *U* = 1474(1) Å$^3$, *Z* = 2, $D_c$ = 1.641 g cm$^{-3}$, μ(Mo-Kα) = 8.377 cm$^{-1}$. Rigaku AFC6S diffractometer, 3124 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, *R* = 4.65, $R_w$ = 5.16%. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

receptor–substrate interaction in the solid state (see Figs. 1, 2).

In both compounds, the primary interaction is the coordination of the unprotonated nitrogen atom, N(1), to Pd *via* a Pd–N σ-bond; 2.166(6) and 2.170(6) Å for $[Pd(L^3)(NH_2NH_3)]^{2+}$ and $[Pd(L^4)(NH_2NH_3)]^{2+}$, respectively. The degree of second-sphere coordination depends on the ability of the $NH_2NH_3^+$ ion to penetrate the different sized crown ether rings and the number of ether oxygen atoms that can potentially act as hydrogen bond acceptors. For $[Pd(L^3)(NH_2NH_3)]^{2+}$, the hydrazinium ion perches over the crown ether ring and there is one hydrogen bond from the bound $NH_2$ group to the first ether oxygen in the crown ether ring, N(1)···O(1) 2.885(8) Å, forming a pseudo-chelate ring while one further H atom of the $NH_3^+$ group hydrogen bonds in a bifurcated fashion to O(2) and O(3); N(2)···O(2) 2.956(9), N(2)···O(3) 2.952(8) Å. This results in a four point interaction between the organopalladium complex and the hydrazinium ion. For $[Pd(L^4)(NH_2NH_3)]^{2+}$, the fit of receptor and substrate is quite remarkable. The $NH_2NH_3^+$ ion is nested in the larger crown ether ring and six hydrogen bonding interactions accompany the Pd–N σ-bond, two to the $NH_2$ group, N(1)···O(1) 2.853(7), N(1)···O(2) 3.005(8) Å, and four to the $NH_3^+$ group, N(2)···O(2) 3.053(8), N(2)···O(3) 2.834(8), N(2)···O(4) 2.782(7), N(2)···O(5) 2.773(8) Å.

The differing degree of secondary interaction between the hydrazinium ion and the two metalloreceptors also has a marked effect on the arrangement of metal cations and anions in the solid state. The crystals of $[Pd(L^3)(NH_2NH_3)][CF_3SO_3]_2$ form $C_2A_4$ units (C = cation, A = anion) in which the four anions are sandwiched between two cations with the crown ether rings forming the outer layers of the unit, while in crystals of $[Pd(L^4)(NH_2NH_3)][BF_4]_2$, the anions are positioned on either side of the cation in a simpler $CA_2$ arrangement.

Binding of the hydrazinium ion *via* simultaneous first- and second-sphere coordination to the metalloreceptors demonstrates that this type of multiple interaction mode can be designed into a receptor and tuned to fit a particular molecule or ion.

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