Co^{II}–N bond lengths. But, the Co–N stretching frequency of Co^{III}(taptacn) is 519 cm^{-1} (identified by an 8-cm^{-1} shift upon deuteriation of the primary amines) compared to 479 cm^{-1} for Co^{III}(tacn)$_2$.[45] The greater force constant can then lead to a greater inner-sphere reorganization energy.

It has been shown recently that the self-exchange parameters of Co$^{3+/2+}$ couples may be treated in the framework of the Marcus–Sutin model for outer-sphere electron transfer.[38] For complexes of the type under consideration the preequilibrium constant (K_0) is 0.04 (I = 0.1 M) and radii (r) are 9.0 Å (with reaction thickness δ_r = 0.8 Å). From these values, a self-consistent set of parameters for the Marcus–Sutin model has been determined for the Co(taptacn)$^{3+/2+}$ couple: ΔG_{in}^* = 13.8 kcal/mol; ΔG_{out}^* = 5.2 kcal/mol, and $d_2 - d_3$ = 0.165 Å, yielding k_{exc} = 0.04 M^{-1} s^{-1} as observed in the present study. The somewhat smaller Δd value calculated for the present complexes is in keeping with the Co(III) species being slightly distorted toward the Co(II) structure when compared to the structure of the Co(tacn)$_2$$^{3+}$ complex. However, a higher inner-sphere reorganization energy is postulated due to the increased force constants, thus rendering the self-exchange rate slower than for Co(tacn)$_2$$^{3+/2+}$.

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Registry No. A, 114928-83-5; B, 114928-81-3; tcetacn, 112995-08-1; taptacn, 114886-07-6; [Ni(taptacn)](ClO$_4$)$_2$, 114928-80-2; [Co^{III}(taptacn)]Cl$_3$, 114928-82-4; Co^{II}(tacn)$_2$$^{2+}$, 91760-59-7; Co^{III}(taptacn)$^{3+}$, 114928-84-6; Co^{II}(sep)$^{2+}$, 63218-22-4; Ni^{III}(taptacn)$^{3+}$, 114928-85-7; Ni(taptacnH$_3$)$^{5+}$, 114928-87-9; Co^{II}(taptacn)$^{2+}$, 114928-88-0; 1,4,7-triazacyclononane, 4730-54-5; acrylonitrile, 107-13-1.

Supplementary Material Available: Tables S1–S5, containing anisotropic temperature parameters for compounds A and B, the calculated fractional coordinates for the hydrogen atoms of compound A, selected interatomic distances for compound B, and ligand bite and torsion angle values related to the trigonal twist (7 pages); Tables S6 and S7, listing calculated and observed structure factors (22 pages). Ordering information is given on any current masthead page.

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(45) Boeyens, J. C. A.; Forbes, A. G. S.; Hancock, R. D.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 2926.

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Crystal and Solution Structure of the Palladium(II) Bis(1,4,7-triazacyclononane) Ion: Evidence for Rapid Fluxional Behavior in a Macrocyclic Complex

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An unusual example of fluxionality at the normally inert Pd(II) center is described. The preparation and X-ray crystal structure of the Pd(non)$_2$$^{2+}$ ion (non = 1,4,7-triazacyclononane) are presented. Pd(non)$_2$(PF$_6$)$_2$ crystallizes in the space group $P2_1/c$ with cell dimensions of a = 7.150 (1) Å, b = 16.675 (6) Å, c = 9.542 (3) Å, and β = 97.37 (2)° (Z = 2). In the solid state the ion displays square-planar geometry, Pd–N = 2.057 Å, with the third (noncoordinated) nitrogen atom in a configuration remote (~3.5 Å) from the metal center and the rings in an anti conformation. However, in solution at ambient temperatures, ^{13}C NMR shows only a single resonance, explicable only by a rapid ring hopping of the Pd(II) around the triaza macrocycle. This is considered to be the first example of such behavior for a Pd(II) amine complex. Temperature-dependence studies have permitted identification of syn and anti conformations in equilibrium ($K_{eq} \approx 2$). Rate data for the interconversion have been obtained, and a possible mechanism is proposed. The fluxional behavior of this ion explains the ready oxidation by air in aqueous medium to a very stable hexacoordinate Pd(III) ion.

Introduction

The importance of the use of small macrocycles such as 1,4,7-triazacyclononane (non) in the maintainance of geometrical configurations of metal complexes is being increasingly recognized. In the bis(ligand) metal complexes, octahedral geometry[1–5] is imposed as a result of the facial disposition of the donor atoms. However, dimeric species[6] of Fe(III) containing a μ-oxo bis(μ-acetato) core, a hemerythrin analogue,[7] and of Mn[8] may be formed where the facially coordinating tridentate ligand effectively caps the outer poles of the dimetal ion core. To date, most of the studies have been made on first-row elements, and much less information is available on second- and third-row congeners.[9–11] In addition to characterization, including X-ray data, a considerable interest has been shown in these species, since not only are they remarkably resistant to acid hydrolysis but also it is possible to prepare complexes in less common oxidation states. Generally, for the couples M(non)$_2$$^{3+/2+}$ (M = Ni,[3,4,12] Fe,[3,13,14] Co[2,15]) there is retention of configuration in the redox reactions. Rates of self-exchange and other redox parameters may be related[16,17] to the changes in the M–N inner coordination sphere distances upon electron transfer.

In this paper, we describe the preparation, crystal structure, and solution magnetic resonance features of the Pd(non)$_2$$^{2+}$ ion. The structure is closely similar to that of the corresponding Pt(II) complex[9] Pt(non)$_2$$^{2+}$, where it is seen that only two of the three

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(1) (a) Yang, R.; Zompa, L. J. *Inorg. Chem.* **1976**, *15*, 1499. (b) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1978**, *28*, L157.
(2) Koyama, H.; Yoshino, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 481.
(3) Wieghardt, K.; Schmidt, K.; Herrmann, W.; Kuppers, H. J. *Inorg. Chem.* **1983**, *22*, 2953.
(4) McAuley, A.; Norman, P. R.; Olubuyide, O. *Inorg. Chem.* **1984**, *23*, 1939.
(5) Kuppers, H. J.; Neves, A.; Pomp, C.; Ventur, D.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2400.
(6) Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 722.
(7) Lippard, S. J. *Chem. Br.* **1986**, 222.
(8) Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230.
(9) Wieghardt, K.; Koppen, M.; Swiridoff, W.; Weiss, J. *J. Chem. Soc., Dalton Trans.* **1983**, 1869.
(10) (a) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Roberts, Y. V.; Lavery, A. I.; Schroder, M. *J. Organomet. Chem.* **1987**, *323*, 261. (b) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Lavery, A. J.; Odulate, M. O.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1987**, 118.
(11) Wieghardt, K.; Herrmann, W.; Koppen, M.; Jibril, I.; Huttner, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1335.
(12) Wieghardt, K.; Walz, W.; Nuber, B.; Weiss, J.; Ozarowski, A.; Stratemeier, H.; Reinen, D. *Inorg. Chem.* **1986**, *25*, 1650.
(13) Boeyens, J. C. A.; Forbes, A. G. S.; Hancock, R. D.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 2926.
(14) Marsh, R. E. *Acta Crystallogr., Sect. B: Struct. Sci.* **1987**, *B43*, 174.
(15) McAuley, A.; Norman, P. R.; Olubuyide, O. *J. Chem. Soc., Dalton Trans.* **1984**, 1501.

donor nitrogens of each macrocycle are coordinated, owing to the strong preference for square planarity associated with d^8 centers, especially for second- and third-row elements. In this regard, the Pd(II) complexes of protonated *cis*-3,5-diaminopiperidine adopt a similar square-planar configuration[18] with the piperidine nitrogen noncoordinating.

Generally, the lability of Pd(II) is intermediate[19] between that of nickel(II) and platinum(II). Several experiments have been carried out to investigate substitution processes, particularly with sterically crowded ligands (e.g., Et_4dien) to force a dissociative pathway.[20] However, a most striking feature of the solution chemistry of the complex ion under consideration is the dynamic nature of the exchange processes at Pd(II). The present study affords a view of ligand exchange at this ion as a result of a proximally positioned coordinating atom located in an axial site as a result of ligand geometry. This provides an unusual example of fluxionality at a Pd(II) metal center, which is normally considered to be square-planar and inert. Relatively few examples are available of such behavior at second- and third-row d^8 complexes. Canty et al.[21] have studied the tripyrazolylborate complexes of palladium(II), which are square-planar but produce NMR spectra consistent with only a single type of pyrazolyl group. Coalescence points are not available for all of the compounds. However, for the palladium $(py)_3CH$ complex a value of ~30 °C is given, which is consistent with an activation energy of ~14.9 kcal/mol for the process. This is relatively high owing to the bulky ligand involved. Similarly, Dixon et al.[22] have employed temperature-dependent ^{31}P NMR to monitor the fluxionality of chloro(triethylphosphine)[tris(diphenylphosphinothioyl)-methyl]platinum(II) and the corresponding bis(triethylphosphine) complex. The exchange process for the chloro compound is postulated to involve one strong Pt–P bond, which remains attached, and the fluxional coordination of the remaining sulfur donors with an activation energy of 13.6 kcal/mol. With the bis(triethylphosphine) complex, a three-site exchange of all of the sulfurs is thought to occur, with an activation energy of 10.9 kcal/mol. In the present study, however, where the ligand is much smaller, σ-bonded, and symmetric, the data do serve to provide a mechanism for the observation that, on aerial or chemical oxidation[23] of the Pd(II) complex, the product is a monomeric palladium(III) species, $Pd(non)_2^{3+}$, of considerable kinetic stability in aqueous media, where ESR evidence is consistent with a hexacoordinate metal center.

Experimental Section

The ligand 1,4,7-triazacyclononane was synthesized by using a modification of the method of Atkins et al.,[24,25] utilizing the high degree of cyclization achieved by the reaction of the disodium salt of *N,N′,N″*-tritosyldiethylenetriamine with the ditosyl derivative of 1,2-ethanediol (tosyl = *p*-tolylsulfonyl).

Synthesis of the palladium(II) complex is best achieved in nonaqueous solvents, although a method for synthesis in aqueous media is also described. $PdCl_2$ (0.50 g, 2.8 mmol) was dissolved in 50 mL of DMSO by heating to 70 °C, with stirring, in an oil bath. The reaction vessel was purged with argon and the solution degassed with by bubbling argon prior to and during the reaction. The condenser was fitted with a drying tube. The ligand, 1,4,7-triazacyclononane (0.90 g, 7.0 mmol), was dissolved in 20 mL of 100% ethanol and degassed as described. This ratio of ligand to palladium (2.5:1) is necessary to ensure formation of the bis(ligand) complex. After all of the $PdCl_2$ had dissolved, the DMSO solution was removed from the oil bath, and before it had cooled significantly, the ethanolic ligand solution was added dropwise over a short period of time (~2 min). The mixture was left stirring while cooling, and after approximately 5 min, a cream-colored precipitate was formed. The solid collected was washed with fresh DMSO, ethanol, and diethyl ether and allowed to air-dry; yield 0.75 g (62%). Anal. Found: C, 32.87; H, 6.79; N, 18.57; Cl, 15.74. Calcd for $C_{12}H_{30}N_6PdCl_2$: C, 33.08; H, 6.94; N, 19.29; Cl, 16.27.

Table I. Crystallographic Parameters for $Pd(non)_2(PF_6)_2$

formula	$C_{12}H_{30}N_6PdP_2F_{12}$
mol wt	654.73
space group	monoclinic, $P2_1/c$
unit cell	
a	7.150 (1) Å
b	16.675 (6) Å
c	9.542 (3) Å
β	97.37 (2)°
vol	1128.3 Å^3
Z	2
D_{calcd}	1.920 g/cm^3
cryst dimens	0.75 × 0.16 × 0.39 mm
μ	9.62 cm^{-1}
radiation	Mo Kα, λ = 0.71069 Å
scan width	1.44°
2θ	0.1–50.0°
no. of rflns	1993
no. of rflns with $I > \sigma(I)$	1711
no. of params	211
stds	0.60; –200; 004 (no decay)
residual electron density	0.8 e/Å^3
max final shift/error	0.26
R, R_w	0.0422, 0.0443

The aqueous preparation used 0.50 g (2.8 mmol) of $PdCl_2$ dissolved in 20 mL of deionized water. The pH was adjusted to 9 by using 2.0 M NaOH. The high pH prevented all of the $PdCl_2$ from dissolving in the solution. The solution was warmed, with stirring, to 50 °C. The ligand, as the hydrochloride salt (1.67 g, 7.0 mmol), was added directly to the $PdCl_2$ solution, where it dissolved rapidly. Heating was continued for 1 h (<50 °C), during which time any remaining $PdCl_2$ dissolved and the solution turned lemon yellow. A black precipitate, assumed to be palladium metal, formed (~0.13 g or ~45% based on $PdCl_2$), which was removed. The yellow supernatant contained two species, the $Pd(non)_2^{2+}$ and the $Pd(non)_2^{3+}$ cations. Upon addition of a dilute solution of ammonium hexafluorophosphate, crystals of $Pd(non)_2(PF_6)_2$ formed, which were used subsequently in the X-ray crystallographic study. Anal. Found: C, 22.33; H, 4.97; N, 12.56. Calcd for $C_{12}H_{30}N_6PdP_2F_{12}$: C, 22.01; H, 4.62; N, 12.84. Upon further standing or upon addition of a saturated NH_4PF_6 solution, the more abundant $Pd(non)_2^{3+}$ cation precipitated. This compound will be discussed in a future publication.

Crystal Data. Crystals were obtained from the slow cooling of a dilute solution of NH_4PF_6 and $Pd(non)_2^{2+}$. The crystal was mounted inside a Lindemann tube and photographed by Weissenberg and precession cameras. The final lattice parameters were obtained from a least-squares refinement of 15 accurately centered, high-angle reflections. The space group was confirmed by the collection of the 0*k*0 reflections, where the expected systematic absences occurred. The data were collected on a Picker four-circle diffractometer, and pertinent crystallographic data are given in Table I. After correction for absorption effects, the structure was solved by using the direct-methods package of SHELX.[26] The palladium and phosphorus atoms were easily locatable, and all other atoms were obtained from the Fourier difference maps following least-squares refinement. The hydrogen atoms were located from the difference map and were included in the final stages of refinement. All non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from the compilations of Cromer and Mann,[27] and corrections for the real and imaginary components of anomalous dispersion were taken from the table of Cromer and Libermann.[28]

NMR. ^1H and ^{13}C NMR spectra were recorded at 250.1 and 62.9 MHz, respectively, by using a Bruker WM250 Fourier transform spectrometer locked to the solvent deuterium resonance. ^{13}C spectra were

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(16) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(17) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(18) Monohar, H.; Schwarzenbach, D.; Iff, W.; Schwarzenbach, G. *J. Coord. Chem.* **1979**, *8*, 213.

(19) Tobe, M. L. *Inorganic Reaction Mechanisms*; Nelson: London, 1972.

(20) Roulet, R.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 2101.

(21) Canty, A. J.; Minchin, N. J.; Engelhardt, L. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 645.

(22) Browning, J.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R. *Inorg. Chem.* **1986**, *25*, 1987.

(23) Fortier, D.; McAuley, A.; Subramanian, S.; Whitcombe, T. Presented at the 30th Congress of IUPAC, Manchester, England, 1985; paper 4PA21.

(24) Atkins, T. J.; Richman, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 2268.

(25) Atkins, T. J.; Richman, J. E.; Oettle, W. F. *Org. Synth.* **1978**, *58*, 86.

(26) Sheldrick, G. M. "SHELX76, Program for Crystal Structure Refinement"; University of Cambridge: Cambridge, U.K., 1976.

(27) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(28) Cromer, D. T.; Libermann, D. A. *J. Chem. Phys.* **1970**, *53*, 1891.

Table II. Fractional Atomic Coordinates and Temperature Parameters[a]

atom	x/a	y/b	z/c	U_{eq}, Å^2
Pd	0 (0)	0 (0)	0 (0)	339 (2)
P	53297 (19)	63837 (8)	84843 (14)	497 (4)
F(1)	5520 (6)	6931 (3)	9839 (4)	92 (2)
F(2)	5961 (8)	5629 (3)	9382 (5)	120 (2)
F(3)	3201 (6)	6221 (3)	8622 (6)	123 (2)
F(4)	7474 (6)	6529 (3)	8305 (5)	112 (2)
F(5)	5133 (5)	5818 (3)	7115 (4)	86 (2)
F(6)	4787 (8)	7139 (3)	7573 (5)	130 (2)
N(1)	1142 (6)	236 (3)	2060 (4)	45 (1)
N(2)	1360 (6)	1046 (3)	−371 (4)	47 (1)
N(3)	−1448 (8)	1652 (4)	1849 (7)	83 (2)
C(4)	2582 (8)	904 (4)	2097 (6)	58 (2)
C(5)	3122 (7)	1028 (4)	692 (6)	55 (2)
C(6)	226 (10)	1796 (4)	−389 (9)	70 (2)
C(7)	−1591 (12)	1738 (6)	343 (9)	87 (3)
C(8)	−1864 (9)	919 (5)	2443 (7)	77 (3)
C(9)	−249 (9)	403 (5)	3056 (6)	63 (2)
H(11)	182 (9)	−15 (3)	225 (7)	5 (2)′
H(21)	177 (10)	97 (4)	−128 (8)	8 (2)′
H(31)	−196 (12)	209 (5)	237 (10)	14 (3)′
H(41)	203 (9)	142 (4)	242 (7)	9 (2)′
H(42)	361 (9)	70 (3)	267 (6)	6 (2)′
H(51)	377 (7)	149 (3)	60 (5)	5 (1)′
H(52)	389 (7)	55 (4)	42 (6)	6 (1)′
H(61)	−12 (9)	176 (4)	−139 (7)	8 (2)′
H(62)	108 (15)	225 (6)	5 (10)	14 (3)′
H(71)	−235 (11)	126 (6)	24 (9)	11 (3)′
H(72)	−225 (11)	223 (5)	10 (8)	11 (3)′
H(81)	−273 (9)	55 (5)	155 (8)	9 (2)′
H(82)	−271 (10)	102 (4)	310 (8)	10 (2)′
H(91)	−84 (14)	−8 (4)	322 (0)	10 (3)′
H(92)	45 (7)	68 (3)	390 (6)	6 (2)′

[a] Estimated standard deviations are given in parentheses. Coordinates are $\times 10^n$, n = 5, 5, 4, 4, 4, and 3 for Pd, P, F, N, C, and H, respectively. Temperature parameters are $\times 10^n$, where n = 4, 4, 3, 3, 3, and 2 for Pd, P, F, N, C, and H, respectively. U_{eq} is the equivalent isotropic temperature parameter, $= {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i a_j)$. Primed values indicate that U_{iso} is given. $T = \exp[-(8\pi^2 U_{iso}(\sin^2\theta)/\lambda^2]$

Table III. Interatomic Distances (Å)[a]

N(1)–Pd	2.068 (4)	C(9)–N(1)	1.487 (7)
N(2)–Pd	2.050 (4)	C(5)–N(2)	1.512 (7)
F(1)–P	1.574 (4)	C(6)–N(2)	1.490 (8)
F(2)–P	1.556 (5)	C(7)–N(3)	1.434 (11)
F(3)–P	1.568 (4)	C(8)–N3)	1.395 (10)
F(4)–P	1.583 (4)	C(5)–C(4)	1.456 (8)
F(5)–P	1.603 (3)	C(6)–C(7)	1.555 (11)
F(6)–P	1.551 (5)	C(9)–C(8)	1.499 (10)
C(4)–N(1)	1.514 (7)		

[a] Estimated standard deviations are given in parentheses.

obtained with broad-band ("noise") irradiation at appropriate frequencies to decouple the protons. Solvents were used without further purification. For the nonaqueous solvents, the solution was saturated with the palladium(II) species at the appropriate temperatures, while a concentration of 0.28 M was used in D_2O.

Simulated NMR spectra were calculated by using UEAITR[29] and NMRPLOT[30] on an IBM 3083 computer with a Tektronix 4013 graphics terminal. The dynamic spectra and line-shape analysis were simulated by using a modification of DNMR3.[31]

Results and Discussion

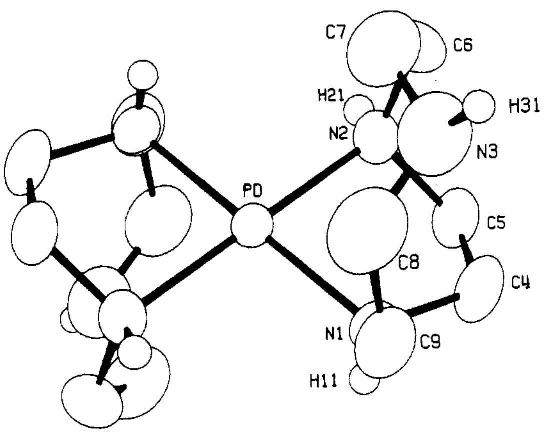

Figure 1. ORTEP diagram of the $Pd(non)_2^{2+}$ cation. Only the hydrogen atoms located on the nitrogens are included for simplicity of view. The Pd–N bond lengths are Pd–N(1) = 2.068 (4) Å and Pd–N(2) = 2.050 (4) Å. The nonbonding distance Pd–N(3) is 3.499 (5) Å.

Table IV. Bond Angles (deg)[a]

N(2)–Pd–N(1)	82.2 (2)	C(4)–N(1)–Pd	110.3 (3)
F(2)–P–F(1)	91.6 (3)	C(9)–N(1)–Pd	115.4 (3)
F(3)–P–F(1)	90.8 (2)	C(9)–N(1)–C(4)	110.9 (5)
F(3)–P–F(2)	91.7 (3)	C(5)–N(2)–Pd	103.9 (3)
F(4)–P–F(1)	91.0 (2)	C(6)–N(2)–Pd	116.5 (4)
F(4)–P–F(2)	88.1 (3)	C(6)–N(2)–C(5)	115.5 (5)
F(4)–P–F(3)	178.2 (2)	C(8)–N(3)–C(7)	120.2 (7)
F(5)–P–F(1)	179.4 (3)	C(5)–C(4)–N(1)	110.0 (4)
F(5)–P–F(2)	87.8 (3)	C(4)–C(5)–N(2)	108.9 (4)
F(5)–P–F(3)	89.0 (2)	C(6)–C(7)–N(3)	120.0 (6)
F(5)–P–F(4)	89.2 (2)	C(7)–C(6)–N(2)	115.3 (6)
F(6)–P–F(1)	88.8 (3)	C(9)–C(8)–N(3)	117.9 (6)
F(6)–P–F(2)	177.6 (3)	C(8)–C(9)–N(1)	113.8 (5)
F(6)–P–F(3)	90.7 (3)		
F(6)–P–F(4)	89.5 (3)		
F(6)–P–F(5)	91.8 (3)		

[a] Estimated standard deviations are given in parentheses.

The structure of $Pd(non)_2(PF_6)_2$ is shown in Figure 1, while the fractional coordinates, bond lengths, and bond angles are contained in Tables II–IV. Temperature factors and other crystallographic information are available as supplementary material. As can be seen from Figure 1, the 1,4,7-triazacyclononane ligand does not adopt an octahedral geometry in the solid state, in keeping with the expected crystal field stabilization of a square-planar complex by a d^8 ion. In this regard, the molecular structure is isostructural with the corresponding Pt(II) ion.[9] However, Zompa[32] has shown that in more acidic media a syn isomer, $[Pd^{II}(non)(Hnon)]^{3+}$], may be formed, where both unbound N donors are on the same side of the PdN_4 plane.

The molecule has a perfect square plane around the palladium, which is necessitated by the 2-fold symmetry axis through the palladium. The structure of the chelating five-membered rings may be compared to the geometry for $Pd(en)_2Cl_2$ (en = ethylenediamine), which has slightly shorter metal–nitrogen bonds (2.037 vs 2.057 Å) but a somewhat larger internal N–Pd–N angle (83.6 vs 82.2°).[33] The remaining structural features are similar, suggesting that the in-plane binding of the palladium is not significantly affected by the remaining bridge in the solid state and that the environment around the palladium is effectively that of a "normal" PdN_4 system.

The remaining (apical) nitrogen is oriented away from the axial coordination site of the palladium, and the necessary ring twisting brings the carbon bridges to within ~3 Å of the palladium with the apical nitrogen (N(3)) at a distance of 3.499 Å. The location of the hydrogen atoms in the Fourier difference maps gives a complete picture of this nitrogen atom and allows for the location of the lone pair. The electrons are oriented away from the d_{z^2} orbital of the palladium, presumably to lower the electron pair repulsion energy that would otherwise be present, although this induces some strain in the molecule. The atoms in the extended bridge have temperature parameters slightly larger than those in

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(29) Johannsen, R. B.; Ferreti, J. A.; Harris, R. K. *J. Magn. Reson.* **1970**, *3*, 84.

(30) Swalen, J. D. *Computer Programs for Chemistry*; Detar, D. F., Ed.; W. A. Benjamin: New York, 1968; Vol. 1.

(31) Kleier, D. A.; Binsch, G. Quantum Chemistry Program Exchange, Program No. 165; University of Indiana: Bloomington, IN, 1969.

(32) Zompa, L. J., private communication.

(33) Wiesner, J. R.; Lingafelter, E. C. *Inorg. Chem.* **1966**, *5*, 1770.

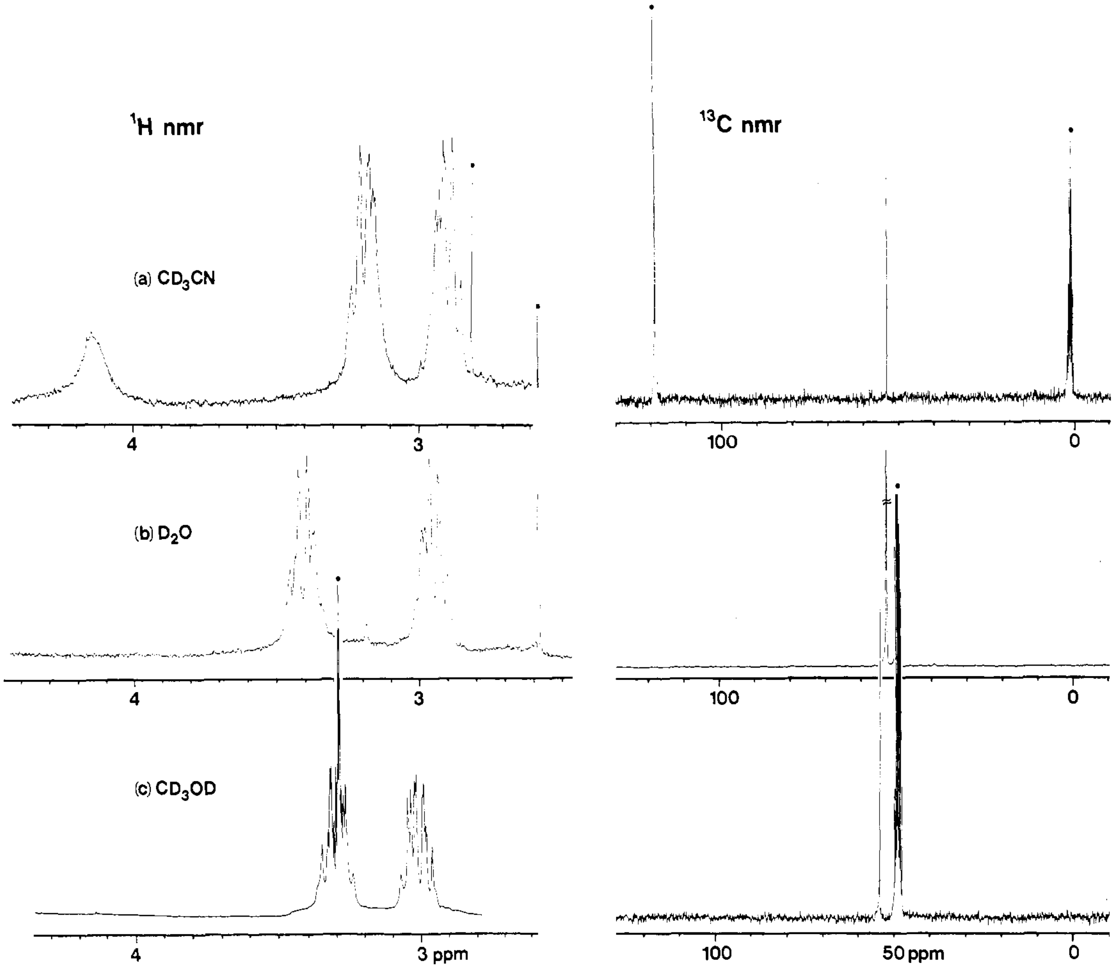

Figure 2. ^{1}H and ^{13}C NMR spectra of the $Pd(non)_2^{2+}$ cation at ambient temperatures in (a) CD_3CN, (b) D_2O, and (c) CD_3OD.

the chelating ring, with the apical nitrogen having an isothermal temperature factor that is almost twice that of the coordinated nitrogens (see Table II). This is a consequence of the flexibility and thermal motion of this portion of the molecule in the solid state and is consistent with a rapid nitrogen inversion rate in solution.

The distance between palladium and N(3) is sufficiently large to permit the atoms to be noninteracting, but the nature of the macrocyclic ligand defines the limit of furthest distance of the apical nitrogen. A value of ~3.5 Å is intermediate between the normal distances for an inner-sphere or coordinated ligand (~2.0 Å) and an outer-sphere or noncoordinated ligand (~4.0 Å). This has unusual and interesting effects upon the solution geometry of the $Pd(non)_2^{2+}$ species, which is demonstrated with NMR spectroscopy.

At ambient temperature, the 62.9-MHz $^{13}C\{^1H\}$ NMR spectrum of $Pd(non)_2^{2+}$ in CD_3CN consists of a single resonance at 52.6 ppm, whereas a well-resolved AA′BB′X multiplet is observed for its 250.1-MHz ^{1}H spectrum (Figure 2a). Rapid exchange of the amino protons with solvent deuterons occurs on dissolution of $Pd(non)_2^{2+}$ in either D_2O or CD_3OD and causes the disappearance of the signal assigned to those protons along with slight shifts in the resonance frequencies for both the ^{13}C and ^{1}H NMR signals (Figure 2b,c). Analysis of the residual symmetrical AA′BB′ subspectrum of the ethylene protons gave chemical shifts of $\delta_a = 3.28$ and $\delta_b = 3.02$ along with the coupling constants $J_{12} = J_{34} = -14.5$ Hz, $J_{13} = J_{24} = 4.2$ Hz, and $J_{14} = J_{23} = 7.2$ Hz. These parameters also successfully simulate the appearance of the ^{1}H spectrum at 90 MHz.

The NMR spectra at ambient temperature are in marked contrast to those anticipated from the crystalline structure and can be explained only by a dynamic process that renders all of the carbon atoms equivalent on the NMR time scale. Resolution into the predicted static spectra was observed in both the ^{1}H and ^{13}C parameters for the nonaqueous solutions of $Pd(non)_2^{2+}$ at lower temperatures. The relatively high freezing point of the acetonitrile rendered it unsuitable for kinetic studies. At −90 °C in CD_3OD, the ^{1}H spectrum is too poorly resolved to identify any spectral pattern. However, at this temperature, the ^{13}C spectrum displays five well-resolved resonances of unequal intensity, at 57.8, 56.9, 55.2, 51.5, and 43.6 ppm. Further decreases in temperature did not enhance signal resolution, as solubility and viscosity effects near the freezing point produced line broadening.

The ambient-temperature ^{1}H NMR spectrum is the result of the diastereotopicity of the two protons in the ethylene bridges due to the stereogenicity of the adjacent nitrogen.[34] Evidence for the dynamic process can be obtained from the AA′BB′ subspectrum, which is not symmetrical, the distortion being due to the contribution of the CC′DD′ structure. Unfortunately, insufficient information is available from the subspectrum analysis to determine the static parameters for both configurations, and hence, the values quoted above are for the dynamically averaged ^{1}H resonances.

The ^{1}H and ^{13}C NMR spectra at ambient and low temperatures do not exhibit any resonances that could be assigned to free ligand in solution, suggesting that the interconversion does not proceed through a dissociative mechanism. The ^{1}H NMR subspectrum confirms that the process must be through an intramolecular pathway since the diastereotopicity of the hydrogens is maintained only if the adjacent nitrogen does not lose its local chirality. Since the chirality is a product of the Pd–N bond, at least one Pd–N bond must be maintained in the dynamic process. The observed diastereotopicity of the geminal methylene protons requires that the original configuration at a coordinated nitrogen be retained on completion of any intramolecular exchange cycle. The only

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(34) Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3320.

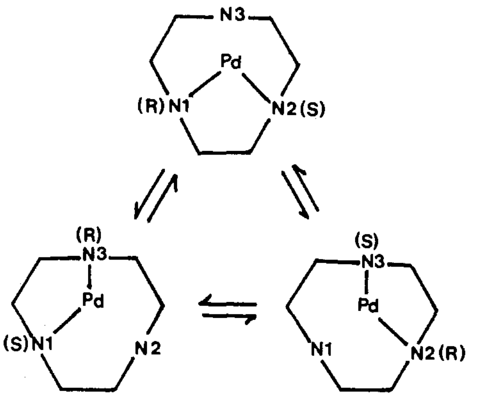

Figure 3. Fluxional process within a single ring with respect to the palladium center. The nitrogens undergo inversion of chirality during the ring movements but always return to the same configuration upon completion of any cycle.

fluxional process that achieves these requirements is that by which the metal effectively hops between any two of the three nitrogen atoms of the cyclic ligand, as illustrated in Figure 3. This can be viewed as an analogue of the ring-whizzing mechanism[35] used in the analysis of metallocenes, but because of the requirement for square planarity at the metal center and the presence of only three ligating atoms in the cyclic triamine, the interaction is better thought of as a "quasi-substitution reaction" within a pseudo-six-coordinate inner sphere.

The temperature-dependent ^{13}C NMR spectra of $Pd(non)_2^{2+}$ can be interpreted as involving two species, since the observed resonances at −90 °C are of unequal intensity. The signals at 57.8, 55.2, and 51.5 ppm arise from the major species while the signals at 56.9 and 43.6 ppm are from a second complex ion. The relative intensities suggest that the two components are in an approximately 2:1 ratio. The signals may be assigned to the anti and syn structures of the $Pd(non)_2^{2+}$ cation, respectively. For the anti structure (Figure 1), the peak at 57.8 ppm is due to carbons of the ethylene bridge between the coordinated nitrogens, that at 55.2 ppm is the carbon next to the coordinated nitrogen in the extended bridge, and the signal at 51.5 ppm is associated with the carbon next to the apical nitrogen. For the syn structure, the peak at 56.9 ppm encompasses both resonances due to the carbons adjacent to the coordinated nitrogens while the resonance at 43.6 ppm arises from the carbon next to the apical nitrogen.[36] The structure of the syn species necessitates that this carbon be in close proximity to the adjacent ligand and to the lone pair of electrons in the d_{z^2} orbital of the palladium, resulting in the larger shift to lower frequencies. All of the resonances are generated by the symmetry equivalence of the pairs of carbon atoms.

The assignment of the observed resonances to two configurations leads to a possible mechanism for the interconversion, part of which is illustrated in Figure 4. In this scheme the anti isomers are designated "A" and the syn isomers "B" with the number designations derived from the nitrogens attached to the palladium. Figure 4 does not give the complete mechanism since it illustrates only the cycle for one ring rotating while the other remains static. Analysis of the mechanism leads to exchange vectors for the configurations, which can be used to obtain a reasonable fit of the observed and simulated spectra if the exchange is between the two configurations (no direct interconversion, i.e. $A_{xx} \rightarrow A_{yy}$) and the rate of exchange is twice as fast from $B_{xx} \rightarrow A_{yy}$ as from $A_{yy} \rightarrow B_{xx}$. The latter condition is necessitated by the observed population difference between the two configurations and results in an effective equilibrium constant of 2. Observed and simulated spectra are illustrated in Figure 5. A least-squares fit to the Eyring equation gives $\Delta G_{298} = 10.2 + 3.8$ kcal/mol.

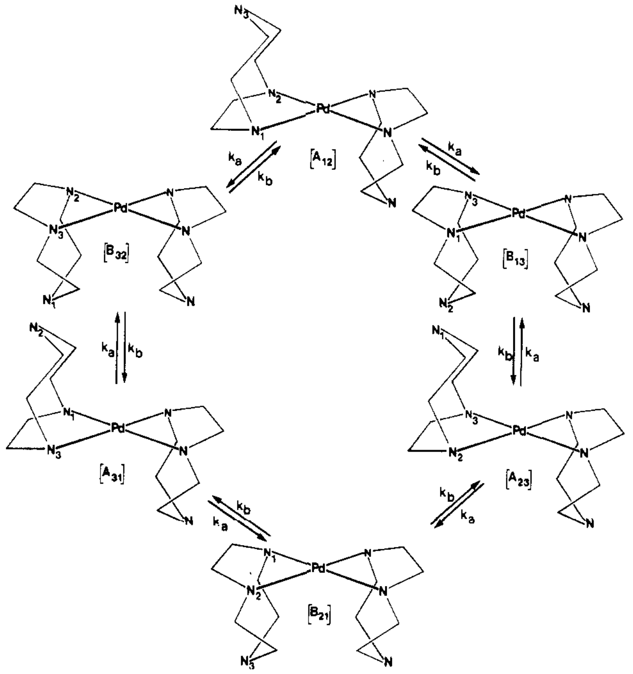

Figure 4. Fluxional process for the $Pd(non)_2^{2+}$ cation involving both ligands in the exchange cycle. The anti (A) and syn (B) configurations interconvert at different rates, designated k_a and k_b.

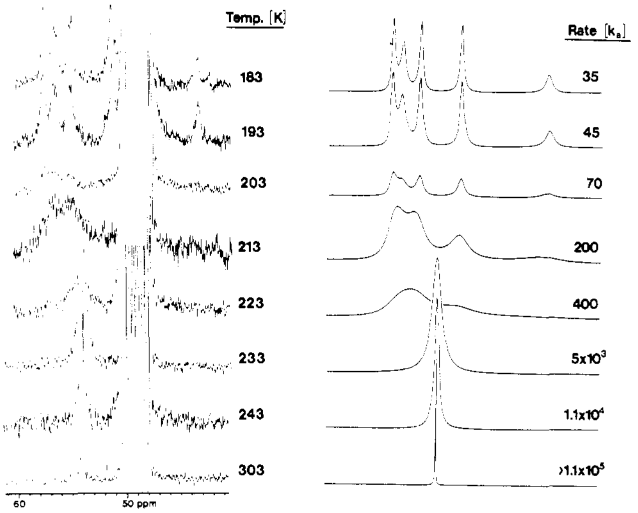

Figure 5. Temperature-dependent ^{13}C NMR spectra, observed vs calculated. The large peak at ~49 ppm is due to CD_3OD. Rates for k_b were always twice those of k_a and are not shown.

The ambient-temperature rate for the conversion of the two configurations is $>1 \times 10^5$ M^{-1} s^{-1}. This rate is substantially faster than that typically observed for substitution processes at a Pd(II) center via a bimolecular process as typified by the ligand substitution reaction for the Pd(dien)X complexes. The rate of substitution[37] for neutral ligands into these complexes is generally <0.1 M^{-1} s^{-1}. The faster rate for $Pd(non)_2^{2+}$ is thus indicative of the enhancement achieved by the pseudo-inner-sphere coordination of the entering ligand, the noncoordinated nitrogen.

The interconversion proceeds through an interchange or an associative-interchange mechanism, typical of palladium(II). The inversion of the nitrogen (N_3 of A_{12}) into an apical location is followed by substitution of this nitrogen onto the palladium, as

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[35] Cotton, F. A. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; Chapter 10.

[36] The other possibility that a third peak belonging to the syn configuration is masked by the methanol peak cannot be totally discounted. Solvents other than methanol are not suitable due to a lack of solubility of the compound (i.e. CD_2Cl_2), the high freezing point of the solvent (i.e. CD_3CN), or the masking of the $Pd(non)_2^{2+}$ resonances by solvent resonances (i.e. C_2D_5OD).

[37] Kotowski, M.; van Eldik, R. *Inorg. Chem.* **1986**, *25*, 3896.

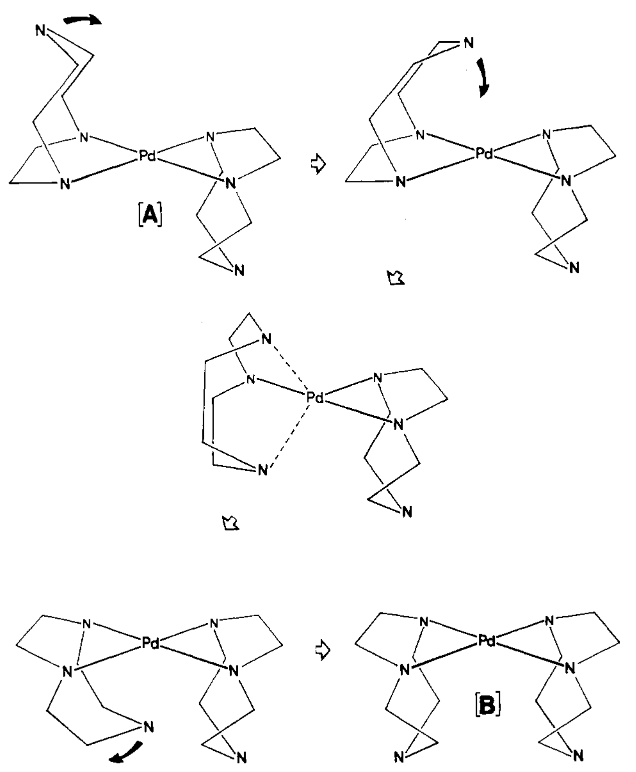

Figure 6. Interconversion of the anti (A) to syn (B) configuration through the inverted ring (A′ and B′) and five-coordinate species (C).

illustrated in Figure 6. The transition state is then a five-coordinate species, with a trigonal-bipyramidal geometry, which then loses a nitrogen (i.e. N_1 to give B_{32}). The resulting structure is the syn species, where both macrocycles are located on the same side of the PdN_4 plane. From B_{32}, the complex can revert to A_{12} or proceed on to A_{31}. The substitution of the apical nitrogen in interconversion necessitates the transition from anti to syn and vice versa. The syn species is thought to be the less stable configuration since it results in a larger interaction between the two macrocyclic rings.

The inversion of the nitrogen center and the substitution onto the palladium may occur as a two-step rather than a concerted process. This would require two activation energies and a two-step mechanism for the interconversion. Ring inversion in cyclooctane has been measured by NMR[38] and a barrier of 8 kcal/mol obtained. Since the unbound segment of the molecule, along with the palladium, constitutes a distorted heterocyclic eight-membered ring, an activation energy of this magnitude may be envisaged for ring inversion, suggesting that, to a large extent, the 10.2 kcal/mol obtained from line-shape analysis represents the energy necessary for ring inversion. In this case, the substitution onto the palladium would represent a lower energy process with an activation energy of ~2 kcal/mol. Although the mechanistic scheme used to interpret the observed NMR spectra does not allow for the determination of two rate processes and no NMR evidence is obtained for an intermediate species of this nature, there is some curvature of the Eyring plot at very low temperatures, which might be explained by a second process or a two-step interconversion.

A low-energy fluxional interconversion has been observed by Dixon[39] for the monodentate phenanthroline complexes of palladium and platinum where coalescence was not observed above −70 °C, suggesting that the location of the lone pair in an axial but nonbonding site produces a very fast interconversion. Since inversion of the apical nitrogen in $Pd(non)_2^{2+}$ leads to a similarly situated amine, the anticipated barrier to the interconversion would be small and a ~2 kcal/mol barrier is viewed as not unreasonable.

As this work was being prepared for publication, evidence of fluxional behavior of a similar type was provided in a Pt(IV) complex.[40] Unlike the complex $Me_3Pt(S_3)^+$ (S_3 = 1,4,7-trithiacyclononane), where NMR spectra show temperature invariance, in the case of $Me_3Pt(S_4)^+$ (S_4 = 1,4,7,10-tetrathiacyclodecane) variable-temperature studies reveal a ligand commutation between the metal-coordinated and uncoordinated sulfur atoms. The Pt(IV) center is octahedral, and a properly positioned donor provides a route to a 1,4-metallotropic shift through a dissociative mechanism. The variable-temperature study led to an activation barrier, ΔG_{298}, of 56.8 ± 0.02 kJ/mol (13.6 kcal/mol). The activation barrier is remarkably small for a d^6 center, which is conventionally viewed as inert. It is of interest here that the corresponding S_3O donor set showed no fluxional behavior.

Ongoing studies of other tridentate macrocycles, such as the N_2S analogue, suggest that the fluxionality of $Pd(non)_2^{2+}$ is not unique. Indeed, the ambient-temperature ^{13}C NMR spectrum of the N_2S complex has just three resonances, as would be expected from the dynamically averaged symmetry-equivalent pairs. Further studies with changes in both the ligand structure and the metal will provide a more detailed picture of the processes involved in the interchange mechanism of these complexes.

The fluxional processes for the $Pd(non)_2^{2+}$ cation serve as a compromise between the square-planar preference of the d^8 metal center and the octahedral preference of the 1,4,7-triazacyclononane ligand. This facilitates the ready oxidation of the complex to the Pd(III) oxidation state, where the octahedral coordination of the macrocycle can be realized.[41]

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Registry No. $Pd(non)_2Cl_2$, 114977-75-2; $Pd(non)_2(PF_6)_2$, 114977-77-4; *syn*-$Pd(non)_2^{2+}$, 110005-45-3.

Supplementary Material Available: Tables containing all thermal parameters, hydrogen positions, and angles and distances associated with the molecule and a diagram illustrating hydrogen positions (8 pages); a table of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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(38) Anet, F. A. L.; Hartman, J. S. *J. Am. Chem. Soc.* **1963**, *85*, 1204.

(39) Dixon, K. R. *Inorg. Chem.* **1977**, *16*, 2618.

(40) Abel, E. W.; Beer, P. D.; Moss, I.; Orrell, K. G.; Sik, V.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1987**, 978.

(41) McAuley, A.; Whitcombe, T. *Inorg. Chem.*, in press.