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Synthesis, and Crystal and Molecular Structure of a Diisopropyl N,N-Diethylcarbamylmethylenephosphonate Palladium Nitrate Complex

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[Diisopropyl N,N-diethylcarbamylmethylenephosphonate]palladium(II) nitrate, $Pd[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2](NO_3)_2$ was prepared from the combination of an acidic aqueous solution of $Pd(NO_3)_2$ and the phosphonate ligand. The complex was isolated and characterized by infrared and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. A single crystal X-ray diffraction analysis of the complex was completed, and it was found to crystallize in the monoclinic space group $P2_1$ *with* $a = 10.430(2)$ Å, $b = 9.124(2)$ Å, $c = 12.190(3)$ Å, $\beta = 111.30(2)°$, $Z = 2$, $V = 1081.8(5)$ Å^3 *and* $\rho_{calcd} = 1.56$ g cm^{-3}. *The structure was solved by standard heavy atom techniques and least-squares refinement converged with* $R_F = 5.3\%$ *and* $Rw_F = 4.9\%$ *on the basis of 2672 independent reflections with* $F \geqslant 5\sigma(F)$. *The crystal contains monomeric units with each Pd(II) atom bonded to two monodentate nitrate ions and one bidentate carbamylmethylenephosphonate ligand forming a square planar coordination geometry about the palladium atom. Several important bond distances include Pd–O(carbonyl) 2.011(5) Å, Pd–O(phosphoryl) 2.031(5) Å, Pd–O(nitrate)$_{avg}$ 1.992(5) Å, P=O 1.499(5) Å and C=O 1.239(9) Å.*

Introduction

Carbamylmethylenephosphonate (CMP) ligands, $(RO)_2P(O)CH_2C(O)NR'_2$, are employed as selective extractants for tripositive actinide ions in acidic radioactive waste solutions [1–9]. Likewise, there is evidence for the formation of CMP complexes with other metal ions present in typical waste solutions. The basic coordination chemistry of CMP ligands with lanthanide ions [10], Th(IV) [11], UO_2^{2+} [12], and Hg(II) [13] has been the subject of recent reports from this laboratory, and these studies have revealed considerable coordination versatility on the part of the CMP ligands. Recently, McIsaac [14] reported that Pd(II) is extracted slowly from acidic nitrate media by $(C_6H_{13}O)_2P(O)CH_2C(O)N(C_2H_5)_2$ (DHDECMP). The extraction data in 1 *M* HNO_3 suggested the formation of a complex $Pd(DHDECMP)_3(NO_3)_2$; however, it was also mentioned that there was evidence for the formation of other complexes. We report here the isolation and spectroscopic characterization of a 1:1 Pd(II)–CMP complex, $Pd[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2](NO_3)_2$. In addition, the determination of the crystal and molecular structure of the complex by single crystal X-ray diffraction methods is described.

Experimental

General Information

The $(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2$, (DiPDECMP), was prepared by literature methods [15] and $Pd(NO_3)_2$ was obtained from Fisher Scientific Co. Infrared spectra were recorded on a Nicolet Model 6000 FT-IR spectrometer by using KBr pellets and liquid thin-films on KBr discs. NMR spectra were recorded on a Varian FT-80 NMR spectrometer operating at 80.0 MHz (^1H), 20.0 MHz (^{13}C) and 32.2 MHz (^{31}P). Samples were contained in 5 mm tubes with an internal deuterium lock solvent. Spectral standards were $(CH_3)_4Si$ (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Elemental analyses were performed by Galbraith Laboratories.

Preparation of the Complex

Typically, 1 mmol of $Pd(NO_3)_2$ was added to a solution containing 1 mmol of $(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2$ in 40 ml of 1 *M* HNO_3, and the solution was stirred overnight. The resulting mixture was filtered and the filtrate evaporated leaving an orange oil. A single crystal suitable for X-ray diffraction analysis was obtained by layering benzene over the oily product. The complex was found to have the composition $PdC_{12}O_{10}N_3PH_{26}$. *Anal.* Calcd.:

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TABLE I. Experimental Data for the X-Ray Diffraction Study of $Pd\{(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2\}(NO_3)_2$.

Crystal System:	monoclinic
Space Group:	$P2_1$
a Å	10.430(2)
b Å	9.124(2)
c Å	12.190(3)
β deg	111.30(2)
V Å^3	1081.8(5)
Z	2
$F(000)$	518
mol. wt.	508.8
ρ(calcd g cm^{-3})	1.56
Diffractometer	Syntex $P3/F$
Radiation	MoK$_\alpha$ (λ = 0.71069 Å)
Temperature	22 °C
Monochromator	highly oriented graphite crystal
Reflections measured	±h, k, l
2θ range	1°–55°
Scan type	θ–2θ
Scan speed	5.0–29.3°/min
Scan range	from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_1) + 1.2]°$
Independent reflections collected	3363
Unique reflections used	2672 with $F \geqslant 5\sigma(F)$
Number of parameters	260
Weighting scheme	$1/[\sigma(F)^2 + gF^2]$, g = 0.00055

C, 28.3; H, 5.1; N, 8.2. Found: C, 29.6; H, 5.7; N, 7.5. Infrared spectrum (cm^{-1}) (thin-film): 2985(m), 2938(m), 1598 (ν_{CO}, s), 1511(s), 1457(m), 1389(m), 1362(m), 1285(s), 1262(s), 1208(w), 1180(m), 1155(m), 1126(w), 1090(m), 1018(s), 971(s), 900(m), 860(w), 826(m), 796(m), 775(m), 733(w), 718(w), 706(w), 678(w), 635(w), 569(m). NMR spectra (D_2O solvent, 27 °C): $^{31}P\{^1H\}$ δ 20.9; $^{13}C\{^1H\}$ δ 166.2 ($^2J_{PC}$ = 6.4 Hz), 73.7 ($^2J_{PC}$ = 7.1 Hz), 44.2, 41.4, 23.6, 13.5, 12.4; ^1H δ 4.93, 4.06 (unresolved multiplet), 2.68 (unresolved multiplet), 0.86, 0.70.

Crystal Structure Determination

A crystal (0.3 mm × 0.3 mm × 0.1 mm) was mounted in a glass capillary and the crystal was centered on a Syntex P3/F automated diffractometer. Determinations of the crystal class, orientation matrix and unit cell dimensions were performed in a standard manner [16]. Data were collected at 22 °C in the θ–2θ scan mode using MoK$_\alpha$ radiation, a scintillation counter and pulse height analyzer. The details of the data collection are presented in Table I. Axial photographs and observed systematic absences, 0k0, k = 2n + 1, are consistent with space groups $P2_1$ and $P2_1/m$. The structure solution proved $P2_1$ to be correct. The data were corrected for Lorentz and polarization effects and the redundant and equivalent reflections were averaged and converted to unscaled $|F_o|$ values. Corrections for absorption were made empirically based upon ψ scans; the minimum and maximum transmission range was 0.609–0.912.

Solution and Refinement of the Structure

All calculations were performed on a R3/SHELXTL structure determination package [16]. Anomalous dispersion terms were included for all atoms with Z > 2. Least-squares refinement in this package uses a blocked cascade algorithm with full-matrix blocks of 103 parameters [17].

The solution and refinement of the structure was based upon 2672 reflections with $F \geqslant 5\sigma(F)$. A sharpened Patterson map was interpreted for Pd, P, O(1) and O(2) positions. Difference Fourier syntheses revealed the locations of the remaining non-hydrogen atoms, and isotropic refinement of these positions gave convergence at R_F = 8.5%. Examination of the U_{iso} values and the difference maps indicated a disorder of the isopropyl group containing C(11)–C(10)–C(12). Secondary positions for C(11) and C(12) were found at about 0.8 Å from the initial positions. The disorder was treated as follows: indivi-

TABLE II. Fractional Coordinates and Thermal Parameters (Å × 10^3) for $Pd[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2](NO_3)_2$.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.15927(5)	0.0000	0.23676(4)	49.4(3)	44.4(2)	39.3(2)	0.6(3)	14.2(2)	−5.9(4)
P	0.1718(2)	0.3111(2)	0.3260(1)	42.3(9)	46.4(9)	36.7(8)	−3.7(7)	12.0(7)	−6.2(8)
N(1)	−0.1975(6)	0.2413(8)	0.1168(5)	43(3)	75(4)	51(3)	9(3)	16(3)	−6(3)
N(2)	0.0406(7)	−0.2707(7)	0.1377(5)	67(4)	45(4)	49(4)	−4(3)	26(3)	0(3)
N(3)	0.4246(6)	−0.0227(15)	0.2279(6)	61(4)	126(9)	62(3)	10(6)	27(3)	4(5)
O(1)	0.2326(5)	0.1611(6)	0.3586(4)	50(3)	50(3)	43(2)	−5(2)	5(2)	4(2)
O(2)	0.2753(5)	0.4292(6)	0.3214(4)	47(3)	63(3)	41(2)	0(2)	6(2)	−17(2)
O(3)	0.1050(5)	0.3670(6)	0.4130(4)	80(4)	59(3)	51(3)	4(3)	37(3)	−1(3)
O(4)	−0.0335(5)	0.0765(6)	0.1950(4)	47(3)	50(3)	60(3)	6(2)	14(2)	−10(2)
O(5)	0.0856(6)	−0.1493(6)	0.1097(4)	96(4)	51(3)	42(3)	−3(2)	25(3)	−17(3)
O(6)	0.0531(7)	−0.2907(7)	0.2385(4)	113(5)	65(4)	49(3)	1(3)	41(3)	−18(4)
O(7)	−0.0109(7)	−0.3574(7)	0.0571(5)	126(5)	55(3)	59(3)	−11(3)	28(3)	−21(4)
O(8)	0.3454(6)	−0.0878(7)	0.2773(5)	66(4)	64(4)	72(4)	4(3)	17(3)	17(3)
O(9)	0.3841(6)	0.0861(9)	0.1733(6)	85(4)	116(6)	90(4)	17(4)	42(4)	−13(4)
O(10)	0.5305(7)	0.0880(14)	0.2390(7)	66(4)	216(11)	150(7)	10(8)	53(5)	33(6)
C(1)	0.0425(7)	0.3185(9)	0.1802(5)	39(4)	55(4)	37(3)	9(3)	7(3)	0(4)
C(2)	−0.0655(7)	0.2050(9)	0.1645(5)	41(4)	60(4)	42(3)	−2(3)	15(3)	−3(3)
C(3)	−0.2502(8)	0.3888(11)	0.0718(7)	52(4)	83(6)	62(4)	11(5)	15(4)	11(5)
C(4)	−0.2711(11)	0.4837(19)	0.1626(9)	98(7)	123(11)	101(7)	19(9)	44(6)	51(9)
C(5)	−0.3004(8)	0.1237(14)	0.1009(9)	41(5)	130(9)	101(7)	23(8)	12(5)	−25(6)
C(6)	−0.3275(14)	0.0382(19)	−0.0098(12)	112(10)	154(16)	128(10)	−15(11)	−3(8)	−8(10)
C(7)	0.4045(6)	0.4587(8)	0.4210(6)	37(3)	69(6)	47(3)	8(3)	3(3)	−4(3)
C(8)	0.5170(8)	0.4608(15)	0.3706(9)	53(5)	133(13)	91(6)	10(7)	30(5)	−18(6)
C(9)	0.3889(9)	0.6013(11)	0.4770(8)	72(6)	68(6)	76(6)	−11(5)	3(5)	−20(5)
C(10)	0.0674(13)	0.2756(12)	0.4974(9)	91(7)	82(7)	61(5)	5(5)	42(5)	−12(6)

Atom	x/a	y/b	z/c	U_{iso}
C(11)	−0.0717(26)	0.2559(35)	0.4729(23)	102(8)
C(12)	0.1378(19)	0.3587(23)	0.6150(15)	78(5)
C(11′)	−0.0833(24)	0.3249(28)	0.4776(20)	76(6)
C(12′)	0.1733(19)	0.2810(22)	0.6152(16)	72(5)

dual positional parameters and U_{iso} were varied as well as the primary and secondary site occupancies g_i such that $g_{primary} + g_{secondary} = 1$; the occupancies refined to 0.521 for C(11), C(12), and 0.479 for C(11′), C(12′) while sharing a common isotropic U. Individual anisotropic thermal parameters were applied to the other nonhydrogen atoms and refinement gave $R_F = 5.9\%$. Hydrogen atom positions were idealized on all carbon atoms with appropriate bond distances and angles, and U_{iso} values for each hydrogen atom except those on C(10), C(11), and C(12) were allowed to vary. The U_{iso} of the disordered hydrogen atoms were set to 1.2 times the last $U_{equiv.}$ of their parent atom. The final least-squares refinement converged to $R_F = 5.3\%$ and $R_{wF} = 4.9\%$. A final difference Fourier synthesis showed three peaks (0.74, 0.56 and 0.52 eÅ^{-3}) at 0.86, 0.88 and 1.75 Å respectively from the Pd atom. The third peak is also 1.2 Å from N(3), O(8) and O(9). The remaining peaks are less than 0.5 eÅ^{-3}. The observed and calculated structure factor amplitudes and hydrogen atom positional parameters are available [18]. The non-hydrogen atom fractional coordinates and thermal parameters are given in Table II.

Results and Discussion

The combination of $(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2$, DiPDECMP, with an equimolar amount of $Pd(NO_3)_2$ in 1 *M* HNO_3 results in the formation of an orange oil *1*. Elemental analyses are consistent with a molecular formula $Pd(DiPDECMP)(NO_3)_2$, and the chemistry is summarized by the following equation:

$$\text{DiPDECMP} + Pd(NO_3)_2 \xrightarrow{1M\, HNO_3} \underset{\mathit{1}}{Pd(\text{DiPDECMP})(NO_3)_2}$$

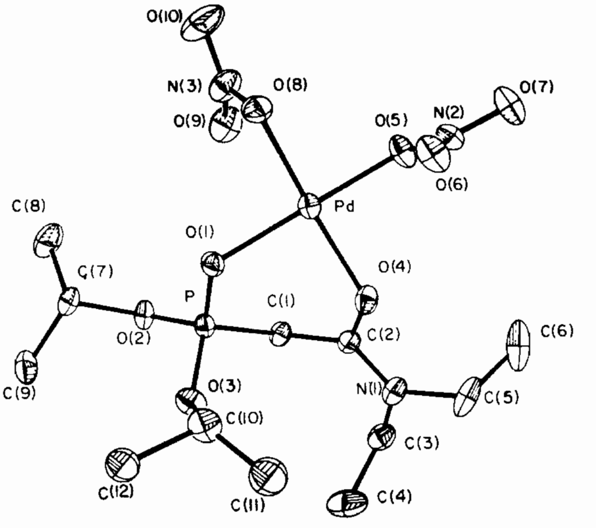

Fig. 1. Molecular geometry and atom labeling scheme for $Pd[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2](NO_3)_2$.

Infrared spectra of the oil show a band at 1598 cm^{-1} which is tentatively assigned as a carbonyl stretching frequency. In the uncoordinated ligand, ν_{CO} is 1644 cm^{-1} and the down-frequency shift upon coordination, $\Delta\nu_{CO}$ = 46 cm^{-1} is typical of metal ion induced shifts in other CMP ligand metal complexes [10–13]. Assignment of the ν_{PO} band in *1* is less certain. There are four strong to medium intensity bands in *1* which appear in the region 1285–1155 cm^{-1}, and the phosphoryl stretching frequency in DiPDECMP is found as a strong absorption at 1253 cm^{-1}. Metal ion coordination of the phosphoryl group of CMP ligands typically results in a down-frequency shift of $\Delta\nu_{PO}$ 30–80 cm^{-1} [10–13]. Therefore, one of the two bands at 1180 and 1155 cm^{-1} in *1* might be assigned to a coordinated P=O group. However, strong bands at 1285 and 1262 cm^{-1} also appear in a region which could indicate the presence of an uncoordinated phosphoryl group. In addition, absorptions in the region 1285–1260 cm^{-1} are often assigned to a mode for coordinated nitrate ion [19]. Clearly, based upon these infrared data alone, the coordination mode of the phosphoryl group in *1* cannot be determined. Metal nitrates also display strong to medium intensity bands at 1530–1480 cm^{-1}, 1035–970 cm^{-1}, and 830–760 cm^{-1}. [19]. By comparison, bands in *1* at 1511 and 971 cm^{-1} may be tentatively assigned to coordinated nitrate group absorptions.

The ^1H, ^{13}C and ^{31}P NMR spectra for *1* may be assigned based upon data for related CMP–metal complexes [10–13]. The $^{31}P\{^1H\}$ spectrum in D_2O solution shows a singlet at 20.9 ppm which is slightly upfield from the resonance in uncoordinated DiPDECMP, 22.0 ppm. The small shift is typical of coordination shifts found previously [10–13], but it cannot be used to unambiguously assign Pd–O(phosphoryl) bonding in *1*. The $^{13}C\{^1H\}$ NMR spectra show resonances centered at 166.2, 73.7, 44.2, 41.4, 23.6, 13.5 and 12.4 ppm which can be assigned to the carbonyl, isopropyl (CH), ethyl (CH_2), ethyl (CH_2), isopropyl (CH_3), ethyl (CH_3) and ethyl (CH_3) carbon atoms, respectively. The amide groups show two methylene and two methyl environments in res-

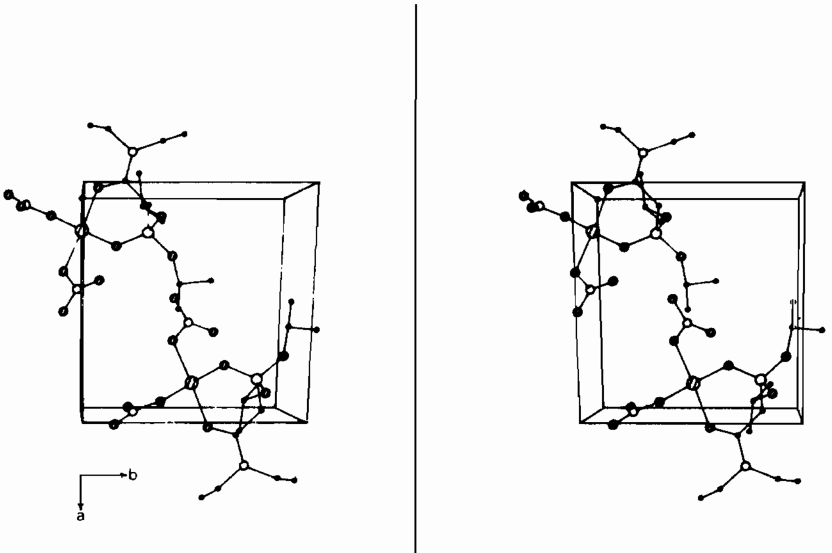

Fig. 2. Stereoview of the molecular packing for $Pd[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2](NO_3)_2$.

TABLE III. Selected Interatomic Distances (Å) for Pd[(i-$C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2](NO_3)_2$.

Pd–O(1)	2.031(5)	O(2)–C(7)	1.474(7)
Pd–O(4)	2.011(5)	O(3)–C(10)	1.483(14)
Pd–O(5)	1.995(5)	C(7)–C(8)	1.509(13)
Pd–O(8)	1.989(6)	C(7)–C(9)	1.506(13)
P–O(1)	1.499(5)	*C(10)–C(11)	1.48(2)
P–O(2)	1.540(6)	*C(10)–C(12)	1.51(2)
P–O(3)	1.552(6)	N(1)–C(3)	1.482(12)
P–C(1)	1.801(6)	N(1)–C(5)	1.480(13)
C(1)–C(2)	1.490(11)	C(3)–C(4)	1.483(17)
C(2)–O(4)	1.239(9)	C(5)–C(6)	1.494(19)
C(2)–N(1)	1.327(9)	N(2)–O(6)	1.201(9)
N(2)–O(5)	1.297(9)	N(2)–O(7)	1.223(8)
N(3)–O(8)	1.327(11)	N(3)–O(9)	1.184(14)
		N(3)–O(10)	1.218(13)

*Averaged distances.

ponse to restricted rotation about the (O)C–N$(C_2H_5)_2$ bond. In D_2O, a resonance for the methylene carbon atom spanning the P=O and C=O groups is not detected. However, in the absence of a deuterium source, the $^{13}C\{^1H\}$ spectrum of *1* in 1 *M* HNO_3 displays a doublet centered at 33.93 ppm, J_{PC} = 137.1 Hz. The collapse of this resonance in D_2O suggests that the methylene carbon atom is a site for facile hydrogen–deuterium exchange [20]. The ^1H NMR spectrum of *1* obtained from a D_2O solution shows resonances at 4.06, 2.68, 0.86 and 0.70 ppm which can be assigned to the isopropyl (CH), ethyl (CH_2), isopropyl (CH_3) and ethyl (CH_3) groups, respectively. Different CH_2 and CH_3 proton environments for the amide ethyl group protons are not resolved, and the protons on the methylene group spanning the P=O and C=O groups are not detected in D_2O solution.

The single crystal X-ray diffraction analysis confirms the molecular formulation of *1* as Pd[(i-$C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2](NO_3)_2$. The structure contains monomeric molecules with two molecules per unit cell. A view of the molecular structure is shown in Fig. 1 and a molecular packing diagram is shown in Fig. 2. Selected interatomic distances and angles are summarized in Tables III and IV. The palladium atom adopts an approximately square planar coordination geometry [21] comprised of two oxygen atoms from two monodentate nitrate ions and the carbonyl and phosphoryl oxygen atoms of a bidentate DiPDECMP ligand. The palladium–O(carbonyl) atom bond distance, Pd–O(4) 2.011(5) Å, is comparable to palladium–oxygen atom distances in two Pd–β-diketonate complexes: [Pd(acac)$_2$(PPh$_3$)] 2.048(10) Å and 2.062(10) Å [22] and [Pd(acac)(PPh$_3$)(CH$_2$COOH)] 2.058(3) Å and 2.064(3) Å [23]. The palladium–O(phosphoryl) atom bond distance, Pd–O(1) 2.031(5) Å is slightly longer than the companion Pd–O(carbonyl) distance. Unfortunately, there do not appear to be comparable Pd–O(phosphoryl) atom distances available in the literature.

The Pd–O(nitrate) bond distances, 1.989(6) Å and 1.995(5) Å (1.992 Å average) are slightly shorter than the Pd–O(nitrate) distances, 2.066 Å, in Pd($Me_2SO)_2(NO_3)_2$ [24]. This complex contains monodentate nitrate ions and sulfur bonded DMSO ligands. The Pd···O(6), 2.877 Å, and Pd···O(9), 2.834 Å, separations are considerably longer than the sum of the ionic radii for Pd(II) and O^{2-} (2.18 Å) yet slightly shorter than the sum of the van der Waal radii (3.1 Å) [25]. The closest intermolecular separation for Pd(II) is Pd–O(7)′ 3.59 Å, which is consis-

TABLE IV. Selected Interatomic Bond Angles (Deg) for Pd[(i-$C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2](NO_3)_2$.

O(1)–Pd–O(4)	90.6(2)	P–C(1)–C(2)	111.2(5)
O(1)–Pd–O(8)	92.1(2)	C(1)–C(2)–O(4)	120.7(6)
		C(1)–C(2)–N(1)	119.9(7)
O(4)–Pd–O(5)	88.4(2)	N(1)–C(2)–O(4)	119.4(7)
O(5)–Pd–O(8)	89.0(2)	Pd–O(4)–C(2)	122.7(5)
Pd–O(1)–P	117.2(2)		
O(1)–P–O(2)	114.5(3)	C(2)–N(1)–C(3)	125.1(7)
O(1)–P–O(3)	111.8(3)	C(2)–N(1)–C(5)	117.6(7)
O(1)–P–C(1)	112.8(3)	N(1)–C(3)–C(4)	112.9(8)
P–O(2)–C(7)	122.7(4)	N(1)–C(5)–C(6)	112.8(10)
P–O(3)–C(10)	125.9(6)	O(5)–N(2)–O(6)	118.9(6)
C(8)–C(7)–C(9)	113.7(8)	O(5)–N(2)–O(7)	115.9(6)
*C(11)–C(10)–C(12)	115.9(13)	O(6)–N(2)–O(7)	125.2(7)
		O(8)–N(3)–O(9)	118.5(8)
		O(8)–N(3)–O(10)	114.7(11)
		O(9)–N(3)–O(10)	126.7(10)

*Averaged angle.

tent with the assumption of a monomeric structural formulation.

The nitrate ions are planar, and the N–O distances containing the coordinated oxygen atoms, N(3)–O(8) 1.327(11) Å and N(2)–O(5) 1.297(9) Å, are longer than the N–O distances containing the uncoordinated oxygen atoms, N(2)–O(6) 1.201(9) Å, N(2)–O(7) 1.223(8) Å, N(3)–O(9) 1.184(14) Å and N(3)–O(10) 1.218(13) Å. A similar effect was observed in $Pd(DMSO)_2(NO_3)_2$ with N–O (coordinated) 1.32(1) Å and N–O (uncoordinated) 1.217(9) Å [24]. The lengthening of the N–O (coordinated) distance in both molecules is greater than the lengthening found in UO_2(DiPDECMP)$(NO_3)_2$, 1.261(9) Å to 1.275(7) Å, in which the nitrate ions are bidentate [12].

The structure of the coordinated DiPDECMP ligand in *1* is similar to that found in other CMP–metal complexes [10–13]. The ligand is in its neutral form and the bond angles about the phosphorus atom indicate a tetrahedral geometry: O(1)–P–O(2) 114.5(3)°, O(1)–O(3) 111.8(3)°, O(1)–P–C(1) 112.8(3)°, O(2)–P–O(3) 106.8(3)°, O(2)–P–C(1) 102.8(3)° and O(3)–P–C(1) 107.5(3)°. The phosphoryl group P–O(1) distance 1.499(5) Å, is longer than the average P=O bond distance, 1.47 Å, in a series of tetrahedral phosphate compounds [26]. The P–O(1) distance in *1* is also longer than the related phosphoryl bond distance in UO_2(DiPDECMP)$(NO_3)_2$ [12] 1.485(5) Å, Th(DEDECMP)$_2$$(NO_3)_4$ [11] 1.478(4) Å, and Sm(DiPDECMP)$_2$$(NO_3)_3$ [10] 1.480(2) Å. In each case, the phosphoryl oxygen atom is bonded to the central metal atom. Clearly, the Pd–O(1) and P–O(1) bond distances are consistent with phosphoryl coordination with Pd(II).

The carbonyl distance in *1*, C(2)–O(4) 1.239(9) Å, is comparable to or slightly shorter than the carbonyl distances in UO_2(DiPDECMP)$(NO_3)_2$ [12] 1.260(8) Å, Th(DEDECMP)$_2$$(NO_3)_4$ [11] 1.256(6) Å and Sm(DiPDECMP)$_2$$(NO_3)_3$ [10], 1.261(3) Å. It is interesting to note that the C(2)–O(4) distance in *1* is most similar to the carbonyl distances in Er(DiPDECMP)$_2$$(NO_3)_3 \cdot H_2O$ [10] 1.239(11) Å and 1.240(11) Å. In that case, the carbonyl oxygen atoms are not bonded to the erbium atom. Instead the carbonyl oxygen atoms are bonded to hydrogen atoms of an erbium coordinated water molecule.

The solid state structural data are fully consistent with a bidentate coordination mode for DiPDECMP toward Pd(II). The solution NMR analysis of *1* indicates the presence of two amide ethyl group environments which is consistent with the bidentate structure in solution. The interesting hydrogen–deuterium exchange process occurring at the methylene group spanning the P=O and C=O has not been fully accounted for, and this process is under study.

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References

1 W. W. Schulz and L. D. McIsaac, 'Transplutonium Elements', W. Müller and R. Lindner, Ed., North Holland, Amsterdam (1976) p. 433.

2 W. W. Schulz, Rept. ARH-SA-203, Atlantic Richfield Co., Hanford, WA, (1974).

3 L. D. McIsaac, J. D. Baker, J. F. Krupa, R. E. LaPointe, D. H. Meikrantz and N. C. Schroeder, Rept. ICP-1180, Allied Chemical Co., Idaho Chemical Programs, Idaho Falls, ID (1979).

4 L. D. McIsaac, J. D. Baker, J. F. Krupa, D. H. Meikrantz and N. C. Schroeder, 'Actinide Separations', *ACS Symposium Ser., 117,* 395 (1980).

5 D. G. Kalina, E. P. Horwitz, L. Kaplan and A. C. Muscatello, *Sp. Sci. Tech., 16,* 1127 (1981).

6 A. C. Muscatello, E. P. Horwitz, D. G. Kalina and L. Kaplan, *Sep. Sci. Tech., 17,* 859 (1981).

7 E. P. Horwitz, A. C. Muscatello, D. G. Kalina and L. Kaplan, *Sep. Sci. Tech., 16,* 417 (1981).

8 E. P. Horwitz, D. G. Kalina and A. C. Muscatello, *Sep. Sci. Tech., 16,* 403 (1981).

9 D. G. Kalina, G. W. Mason and E. P. Horwitz, *J. Inorg. Nucl. Chem., 43,* 159 (1981).

10 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta, 61,* 155 (1982).

11 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chem., 21,* 261 (1982).

12 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chem.,* accepted for publication.

13 S. M. Bowen, E. N. Duesler, R. T. Paine and C. F. Campana, *Inorg. Chim. Acta, 59,* 53 (1982).

14 L. D. McIsaac, *Sep. Sci. Tech.,* in press.

15 T. H. Siddall, *J. Inorg. Nucl. Chem., 25,* 883 (1963).

16 The P3/F and R3 hardware configuration has been described: C. F. Campana, D. F. Sheppard and W. N. Litchman, *Inorg. Chem., 19,* 4039 (1981). Crystal centering, autoindexing, cell parameter refinement and axial photograph programs are those described in the 'Nicolet P3/R3 Operations Manual', Nicolet XRD Corp. 1980. All calculations and plots were performed with the SHELXTL-Revision 3. G. M. Sheldrick, 'Nicolet SHELXTL Operations Manual', 1981. SHELXTL uses scattering factors compiled in 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, U.K. (1968).

17 A general description of the least squares algebra is found in 'Crystallographic Computing', F. R. Ahmed, S. R. Hall and C. P. Huber, Ed., Munksgaard, Copenhagen (1970) p. 187.

18 Supplementary data.

19 K. Nakamoto, 'Infrared Spectra of Inorganic and Organometallic Compounds', Wiley, New York, N.Y., 1963.

20 The details of the hydrogen–deuterium exchange in *1* as a function of solvent and acidity are currently under study.

21 A listing of least-squares atomic planes calculated for the palladium–oxygen atom plane and the nitrate ion planes is available from RTP.

22 M. Horika, Y. Kai, N. Yasuoka and N. Kasai, *J. Organometal. Chem., 72,* 441 (1974).

23 Y. Zenitani, K. Inoue, Y. Kai, N. Yasuoka and N. Kasai, *Bull Chem. Soc. Japan, 49,* 1531 (1976).

24 D. A. Langs, C. R. Hare and R. G. Little, *J. Chem. Soc. Chem. Commun.,* 1080 (1967).

25 J. E. Huheey, 'Inorganic Chemistry, Principles of Structure and Reactivity', Harper and Row, New York, N.Y., 1978.

26 D. E. C. Corbridge, 'The Structural Chemistry of Phosphorus', Elsevier, Amsterdam, 1974.