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Coordination Chemistry of 2-Diethylphosphonato-4,6-dipiperidino-1,3,5-triazine with Uranyl Nitrate

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Abstract

The known ligand, 2-diethylphosphonato-4,6-dipiperidino-1,3,5-triazine has been prepared and the crystal and molecular structure determined by single crystal X-ray diffraction techniques. The molecule crystallized (−30 °C) in the monoclinic space group $P\bar{1}$ (No. 2) with $a = 8.698(3)$, $b = 10.064(4)$, $c = 12.798(5)$ Å, $\alpha = 67.34(3)$, $\beta = 77.08(3)$, $\gamma = 68.01(3)°$, $Z = 2$, $V = 954.5(6)$ Å^3 and $\rho_{calc} = 1.33$ g cm^{-3}. The structure was solved by direct methods and blocked least-squares refinement converged to $R_F = 4.9\%$ and $R_{wF} = 5.2\%$ on 295 variables and 2995 unique reflections with $F > 3\sigma(F)$. Selected bond distances for the ligand include: P–C(1) 1.834(2) Å, P=O 1.452(2) Å and C–N(ring)$_{avg}$ 1.343(3) Å. The complex $UO_2(NO_3)_2\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}_2$ was obtained from a mixture of $UO_2(NO_3)_2 \cdot 6H_2O$ and the ligand in a 1:2 ratio and characterized by spectroscopic methods. The crystal and molecular structure of the compound was determined by single crystal X-ray diffraction methods. The molecule crystallized (20 °C) in the monoclinic space group $P\bar{1}$ (No. 2) with $a = 10.050(2)$, $b = 10.628(2)$, $c = 12.464(2)$ Å, $\alpha = 73.96(1)$, $\beta = 70.25(1)$, $\gamma = 75.32(3)°$, $Z = 1$, $V = 1185.2(3)$ Å^3, and $\rho_{calc} = 1.63$ g cm^{-3}. The structure was solved by heavy atom methods and blocked least squares refinements converged to $R_F = 3.4\%$ and $R_{wF} = 3.6\%$ on 286 variables and 5271 unique reflections with $F > 3\sigma(F)$. The complex contains a linear UO_2^{2+} group bonded to two bidentate nitrate ions and the phosphoryl groups of two *trans* situated phosphonate ligands. Several important bond distances include: U=O 1.764(5) Å, U–O(phosphoryl) 2.381(3) Å, U–O(nitrate)$_{avg}$ = 2.514(3) Å, P=O 1.472(4) Å, P–C(1) 1.817(4) Å, C–N(ring)$_{avg}$ 1.337(6) Å.

Introduction

We have interest in developing methods for immobilizing ligand fragments on polymer backbones which, in turn, may function as useful metal ion separations materials. In this effort, we have recently reported on the attachment of carbamoylmethylphosphonate ligands, known to be good liquid–liquid extrants for actinide(III) ions [1–3] to polystyrene–divinylbenzene copolymer, and on the extraction properties of the resulting functionalized polymer [4]. The results of that study encouraged us to consider other polymeric supports, and triazine polymers based upon the cyanuric chloride monomer seemed to offer some particularly attractive features. However, before examining the polymer chemistry, selected solution coordination chemistry of appropriately functionalized triazine monomers was explored. We report here the coordination chemistry of the known 2-diethylphosphonato-4,6-dipiperidino-1,3,5-triazine [5] (**1**) with uranyl nitrate.

Experimental

The ligand was prepared essentially as described in the literature [5], but additional characterization data are provided. Uranyl nitrate was obtained from Alfa Products (Ventron). Infrared spectra were recorded on a Nicolet 6000 FTIR spectrometer, and samples were prepared as KBr pellets. NMR spectra were recorded on Varian FT-80 and GE NT-360 spectrometers. The spectral standards were 85% H_3PO_4 (^{31}P) and $(CH_3)_4Si$ (^{13}C, ^1H), and resonances downfield of the standard were assigned positive chemical shifts, δ. Elemental analyses were obtained by R. Ju of the UNM Chemical Analysis Laboratory.

Characterization of $\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}$ *(1)*

Colorless crystals. Mpt 104–106 °C. *Anal.* Calc. for $PO_3N_5C_{17}H_{30}$: C, 53.26; H, 7.89; N, 18.27. Found: C, 52.33; H, 7.70; N, 18.11%. Infrared spectrum (cm^{-1}, KBr): 1551 (ν_{CN}), 1227 (ν_{PO}), 979 (ν_{POC}). Mass spectrum (*m*/*e*, ion): 384 ($M + 1^+$), 383 (M^+), 354 ($M - C_2H_5^+$), 327 ($M - C_4H_8^+$), 300, 275, 246. NMR spectra: $^{31}P\{^1H\}$ ($CHCl_3$) δ 6.0; $^{13}C\{^1H\}$ ($CDCl_3$) δ 169.4 ($CP\,^1J_{PC} = 268.7$ Hz),

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TABLE I. Experimental Data for the X-ray Diffraction Study of $\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}$ (1) and $UO_2(NO_3)_2\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}_2$ (2)

	1 (at −30 °C)	2 (at 20 °C)
(a) Crystal parameters		
Formula	$PO_3N_5C_{17}H_{30}$	$UP_2O_{14}N_{12}C_{34}H_{60}$
Crystal system	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.698(3)	10.050(2)
b (Å)	10.064(4)	10.628(2)
c (Å)	12.798(5)	12.464(2)
α (°)	67.34(3)	73.96(1)
β (°)	77.08(3)	70.25(1)
γ (°)	68.01(3)	75.32(3)
Z	2	1
V (Å^3)	954.5(6)	1185.2(3)
Molecular weight (g mol^{-1})	383.43	1161.0
ρ_{calc} (g cm^{-3})	1.33	1.63
μ (Mo Kα) (cm^{-1})	1.65	335.2
F(000)	412	582
(b) Data collection		
Diffractometer	Syntex P3/F	
Radiation	Mo Kα (λ = 0.71069 Å)	
Monochromator	highly oriented graphite crystal	
Reflections measured	$\pm h$ $\pm k$ $\pm l$	$\pm h$ $\pm k$ $\pm l$
2θ limits	2–50°	2–55°
Scan type	ω	θ–2θ
Scan speed (deg min^{-1})	5–30	6–30
Scan range	from [ω(0) − 1.0]° to [ω(0) + 1.0]°	from [2θ(Kα_1) − 1.2]° to [2θ(Kα_2) + 1.4]°
Background measurements	stationary crystal and counter; at the beginning and end of each scan; background counting time/total scan time 0.5	
Standard reflections	3/123	3/123
Reflections collected	5053	11238
Unique, space group allowed reflections	3359	5282
Reflections used in refinement $F > 3\sigma(F)$	2995	5271
Weighting scheme: $1/[\sigma(F)^2 + gF^2]$ g =	0.00029	0.00191

163.1 (CNP, $^2J_{CP}$ = 22.0 Hz), 63.3 (CH_2O, $^2J_{CP}$ = 6.2 Hz), 43.8 (pip)[†], 25.4 (pip), 24.4 (pip), 16.0 (CH_3; $^3J_{PC}$ = 6.4 Hz); ^{1}H ($CDCl_3$) δ 4.26 (d of quar. CH_2O, J_{PH} = 7.1 Hz, J_{HH} = 7.0 Hz), 3.68 (pip), 1.58 (pip), 1.49 (pip), 1.31 (t, CH_3, J_{HH} = 7.0 Hz).

Preparation of the Complex $UO_2(NO_3)_2\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}_2$ (2)

The complex was prepared by combination of 2.0 mmol (1.0 g) $UO_2(NO_3)_2 \cdot 6H_2O$ with 4.0 mmol (1.5 g) of the ligand in 50 ml ethanol. The mixture was stirred and the solvent allowed to evaporate slowly in air. The resulting residue was washed quickly with dry diethyl ether (2 × 5 ml). The complex was then recrystallized from ethanol and isolated as pale yellow crystals. *Anal.* Calc. for $UP_2O_{14}N_{12}C_{34}H_{60}$: C, 35.18; H, 5.21; N, 14.48. Found: C, C, 35.62; H, 5.43; N, 13.80%. Infrared spectrum (cm^{-1}, KBr) 2939(s), 1559(s), 1520(s), 1492(s), 1445(s), 1280(m), 1230(s), 1193(s), 1031(s), 933(s). NMR spectrum: ^{31}P{^{1}H} ($CHCl_3$) δ 7.9.

Crystal Structure Determinations

Ligand

A colorless crystal (0.18 × 0.23 × 0.69 mm), shaped as an elongated rectangular prism, was sealed in a glass capillary. The crystal was centered on a Syntex P3/F automated diffractometer, and the determinations of crystal class, orientation matrix and unit cell dimensions were performed in a standard manner*. Data were collected in a ω scan mode with use of Mo Kα radiation, a scintillation counter and a pulse height analyzer. A summary of data collection parameters appears in Table I. Exami-

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[†] Abbreviations used in the text include: pip = piperidino, ET = ethyl, i-Pr = isopropyl, Ph = phenyl.

*Programs used for centering reflections, autoindexing, refinement of cell parameters, and axial photographs are those described in ref. 6.

TABLE II. Fractional Coordinates and Thermal Parameters for $\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}$[a]

Atom	*x/a*	*y/b*	*z/c*	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
P	−0.04543(7)	0.76364(6)	0.23613(5)	0.0303(3)	0.0207(3)	0.0362(3)	−0.0120(2)	−0.0047(2)	−0.0057(2)
O(1)	0.0673(2)	0.7821(2)	0.29377(15)	0.0444(9)	0.0414(9)	0.0584(11)	−0.0249(8)	−0.0142(8)	−0.0118(7)
O(2)	−0.2064(2)	0.7292(2)	0.30927(13)	0.0319(8)	0.0349(8)	0.0444(9)	−0.0176(7)	−0.0040(7)	−0.0041(7)
O(3)	−0.1187(2)	0.9113(2)	0.13500(14)	0.0496(10)	0.0235(7)	0.0493(10)	−0.0134(7)	−0.0172(8)	−0.0034(7)
C(1)	0.0553(2)	0.6094(2)	0.1762(2)	0.019(1)	0.021(1)	0.033(1)	−0.009(1)	−0.005(1)	−0.004(1)
N(2)	0.0738(2)	0.4698(2)	0.25115(14)	0.0247(8)	0.0197(8)	0.0302(9)	−0.0089(7)	−0.0034(7)	−0.0049(7)
C(3)	0.1529(2)	0.3593(2)	0.2033(2)	0.018(1)	0.020(1)	0.028(1)	−0.006(1)	−0.005(1)	−0.005(1)
N(4)	0.2091(2)	0.3833(2)	0.09381(13)	0.0252(8)	0.0192(8)	0.0247(9)	−0.0046(7)	−0.0036(7)	−0.0062(7)
C(5)	0.1842(2)	0.5299(2)	0.0282(2)	0.018(1)	0.021(1)	0.029(1)	−0.005(1)	−0.004(1)	−0.007(1)
N(6)	0.1040(2)	0.6498(2)	0.06641(14)	0.0241(8)	0.0192(8)	0.0347(10)	−0087(7)	−0.0031(7)	−0.0051(7)
N(7)	0.1785(2)	0.2131(2)	0.27342(14)	0.0322(9)	0.0176(8)	0.0236(9)	−0052(7)	−0.0032(7)	−0.0046(7)
C(8)	0.1104(3)	0.1746(2)	0.3923(2)	0.035(1)	0.025(1)	0.027(1)	−0.008(1)	−0.002(1)	−0.007(1)
C(9)	0.2384(3)	0.0434(3)	0.4673(2)	0.051(1)	0.030(1)	0.027(1)	−0.003(1)	−0.010(1)	−0.008(1)
C(10)	0.3014(3)	−0.0921(2)	0.4264(2)	0.053(1)	0.024(1)	0.035(1)	−0.001(1)	−0.011(1)	−0.002(1)
C(11)	0.3720(3)	−0.0464(2)	0.3027(2)	0.036(1)	0.020(1)	0.041(1)	−0.008(1)	−0.004(1)	−0.003(1)
C(12)	0.2430(3)	0.0863(2)	0.2294(2)	0.038(1)	0.020(1)	0.026(1)	−0.006(1)	−0.002(1)	−0.008(1)
N(13)	0.2429(2)	0.5608(2)	−0.08200(14)	0.0300(9)	0.0185(8)	0.0273(9)	−0.0033(7)	0.0004(7)	−0.0059(7)
C(14)	0.3342(3)	0.4420(2)	−0.1327(2)	0.036(1)	0.024(1)	0.028(1)	−0.008(1)	−0.003(1)	−0.010(1)
C(15)	0.5007(3)	0.4605(2)	−0.1913(2)	0.030(1)	0.032(1)	0.030(1)	−0.012(1)	−0.002(1)	−0.007(1)
C(16)	0.4788(3)	0.6197(2)	−0.2775(2)	0.033(1)	0.039(1)	0.028(1)	−0.007(1)	−0.000(1)	−0.018(1)
C(17)	0.3802(3)	0.7384(2)	−0.2211(2)	0.040(1)	0.028(1)	0.030(1)	−0.002(1)	−0.008(1)	−0.016(1)
C(18)	0.2163(3)	0.7163(2)	−0.1621(2)	0.033(1)	0.021(1)	0.032(1)	−0.001(1)	−0.007(1)	−0.005(1)
C(19)	−0.2055(4)	0.6397(3)	0.4286(2)	0.063(2)	0.059(2)	0.034(1)	−0.022(1)	0.002(1)	−0.027(1)
C(20)	−0.2780(3)	0.5180(3)	0.4562(2)	0.047(1)	0.048(1)	0.47(1)	−0.020(1)	0.005(1)	−0.019(1)
C(21)	−0.2310(4)	0.9195(3)	0.0635(3)	0.078(2)	0.032(1)	0.077(2)	−0.021(1)	−0.046(2)	0.004(1)
C(22)	−0.3165(3)	1.0739(2)	−0.0010(2)	0.051(2)	0.031(1)	0.064(2)	−0.012(1)	−0.022(1)	−0.009(1)

[a] The anisotropic temperature factor exponent takes the form: $-2\pi^2[U(11)ha^{*2} + U(22)kb^{*2} + U(33)lc^{*2} + 2(U(23)kb^*lc^* + U(13)ha^*lc^* + U(12)ha^*kb^*]$.

nation of the standard reflections showed no signs of crystal decay. Redundant and equivalent reflections were averaged and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects. Absorption was considered to be small, so a correction for absorption was not made. The structure was solved by direct methods, and calculations were performed using SHELXTL (Rev. 4)[**]. The best E-map gave trial positions for all non-hydrogen atoms. Blocked least-squares refinements[†] of the positional and individual isotropic thermal parameters converged with $R_F = 12.3\%$. Subsequent anisotropic refinements on the non-hydrogen atoms gave $R_F = 9.3\%$. Inclusion of the hydrogen atoms (positions varied, U_{iso} fixed at 1.2 times U_{eq} of the parent atom) gave $R_F = 4.9\%$ and $R_{wF} = 5.2\%$ with 295 variables and 2995 unique data with $F > 3\sigma(F)$. A final difference map showed peaks 0.47, 0.44 and 0.38 e Å^{-3} located 1.07 Å from O(2), 1.03 Å from O(3) and 0.93 Å from C(21), respectively. The observed and calculated structure factors and hydrogen atom positional parameters are available from the authors. Non-hydrogen atom positional and thermal parameters and bond distances and angles are listed in Tables II and III.

Complex

A pale yellow crystal (0.10 × 0.30 × 0.40 mm) shaped as a transparent plate was mounted on a fiber, and crystal preparation and data collection were performed as described above and as summarized in Table I. Examination of the standard reflections showed no sign of crystal decay. Redundant and equivalent data were averaged and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects: *R*(merge) = 0.97%. An absorption correction was applied based on ψ

[**] The SHELXTL package of programs for calculations and plots is described in ref. 7a. SHELXTL uses scattering factors and anomalous dispersion terms taken from ref. 7b.

[†] A general description of the least-squares algebra is found in ref. 8. The least-squares refinement minimizes $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F)^2 + gF^2]$, $R_F = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$, $R_{wF} = [\Sigma|F_o| - |F_c|)^2/\Sigma wF_o]^{1/2}$, and the goodness of fit GOF $= [w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, were NO is the number of observations and NV is the number of variables.

TABLE III. Structural Parameters for $\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}$

Bond lengths (Å)			
P–O(1)	1.452(2)	P–O(2)	1.576(2)
P–O(3)	1.571(1)	P–C(1)	1.834(2)
O(2)–C(19)	1.444(3)	O(3)–C(21)	1.442(5)
C(1)–N(2)	1.335(2)	C(1)–N(6)	1.319(3)
N(2)–C(3)	1.360(3)	C(3)–N(4)	1.335(2)
C(3)–N(7)	1.358(2)	N(4)–C(5)	1.347(2)
C(5)–N(6)	1.361(3)	C(5)–N(13)	1.344(3)
N(7)–C(8)	1.459(3)	N(7)–C(12)	1.462(3)
C(8)–C(9)	1.519(3)	C(9)–C(10)	1.515(4)
C(10)–C(11)	1.520(3)	C(11)–C(12)	1.518(3)
N(13)–C(14)	1.462(3)	N(13)–C(18)	1.467(2)
C(14)–C(15)	1.518(3)	C(15)–C(16)	1.524(3)
C(16)–C(17)	1.517(3)	C(17)–C(18)	1.509(3)
C(19)–C(20)	1.473(5)	C(21)–C(22)	1.439(3)
Bond angles (°)			
O(1)–P–O(2)	116.7(1)	O(1)–P–O(3)	112.2(1)
O(2)–P–O(3)	102.8(1)	O(1)–P–C(1)	112.6(1)
O(2)–P–C(1)	104.9(1)	O(3)–P–C(1)	106.6(1)
P–O(2)–C(19)	121.8(2)	P–O(3)–C(21)	122.4(2)
P–C(1)–N(2)	114.9(2)	P–C(1)–N(6)	116.5(1)
N(2)–C(1)–N(6)	128.6(2)	C(1)–N(2)–C(3)	112.8(2)
N(2)–C(3)–N(4)	125.1(2)	N(2)–C(3)–N(7)	117.0(2)
N(4)–C(3)–N(7)	117.9(2)	C(3)–N(4)–C(5)	115.7(2)
N(4)–C(5)–N(6)	124.3(2)	N(4)–C(5)–N(13)	118.3(2)
N(6)–C(5)–N(13)	117.4(2)	C(1)–N(6)–C(5)	113.6(2)
C(3)–N(7)–C(8)	122.3(2)	C(3)–N(7)–C(12)	121.7(2)
C(8)–N(7)–C(12)	114.7(2)	N(7)–C(8)–C(9)	110.6(2)
C(8)–C(9)–C(10)	110.8(2)	C(9)–C(10)–C(11)	110.1(2)
C(10)–C(11)–C(12)	110.6(2)	N(7)–C(12)–C(11)	110.9(2)
C(5)–N(13)–C(14)	122.7(2)	C(5)–N(13)–C(18)	122.9(2)
C(14)–N(13)–C(18)	114.4(2)	N(13)–C(14)–C(15)	110.5(2)
C(14)–C(15)–C(16)	111.2(2)	C(15)–C(16)–C(17)	110.2(2)
C(16)–C(17)–C(18)	111.7(2)	N(13)–C(18)–C(17)	110.6(2)
O(2)–C(19)–C(20)	111.8(3)	O(3)–C(21)–C(22)	112.0(3)

scans using a laminar model with 001 as the thin face: R before correction 8.6%; R after correction 1.83%; maximum and minimum transmission factors 0.756 and 0.447. The structure was solved by standard heavy atom techniques using a sharpened Patterson map. The uranium atom was arbitrarily placed at 0.5.5.5, and the difference map, obtained by phasing on this atom, gave the positions of the remaining non-hydrogen atoms. Blocked least-squares refinements of the positional and isotropic thermal parameters converged with $R_F = 8.1\%$. Anisotropic refinement of the non-hydrogen atoms gave $R_F = 3.7\%$. Inclusion of the hydrogen atoms in fixed positions with U_{iso} set to 1.2 times U_{eq} of the parent atom gave a final refinement with $R_F = 3.4\%$ and $R_{wF} = 3.6\%$ on 286 variables and 5271 unique data with $F > 3\sigma(F)$. A final difference map showed one peak, 2.0 e Å^{-3}, 0.96 Å from the uranium atom. The tables of structure factor amplitudes and hydrogen atom positional parameters are available from the authors. Non-hydrogen atom positional and anisotropic thermal parameters are given in Table IV and bond distances and angles are summarized in Table V.

Results and Discussions

The synthesis of the functionalized triazine ligand **1** was first reported by Shaw and coworkers [5], and it may be prepared in good yield according to the following scheme.

$$C_3N_3Cl_3 + P(OEt)_3 \xrightarrow[\Delta]{(1)\ \text{benzene/pet. ether}\quad (2)\ C_5H_{10}N} C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)] + EtCl$$

1

Some characterization data for **1** were presented in the first report [5]; however, additional data are provided here. The air stable, crystalline solid displays a parent ion and expected fragmentation pattern in

TABLE IV. Fractional Coordinates and Thermal Parameters for $UO_2(NO_3)_2\{C_3N_3(C_5H_{10}N)_2[EtO)_2P(O)]\}_2$

Atom	x/a	y/b	z/c	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
U(1)	0.50000	0.50000	0.5000	0.0383(1)	0.0296(1)	0.0323(1)	−0.0069(1)	−0.0049(1)	−0.0059(1)
O(4)	0.4206(4)	0.5059(4)	0.3919(3)	0.0653(19)	0.0548(18)	0.0580(19)	−0.0072(15)	−0.0313(16)	−0.0105(15)
P	0.31487(10)	0.20351(9)	0.66089(9)	0.0407(4)	0.0329(4)	0.0395(5)	−0.0058(4)	−0.0058(4)	−0.0046(3)
O(1)	0.3893(4)	0.3178(3)	0.6248(3)	0.0556(17)	0.0388(14)	0.0567(19)	−0.0046(13)	−0.0005(14)	−0.0140(12)
O(2)	0.2214(4)	0.2042(4)	0.5836(3)	0.0657(19)	0.0531(18)	0.0535(18)	−0.0145(15)	−0.0249(16)	0.0001(15)
O(3)	0.4236(3)	0.0716(3)	0.6565(3)	0.0448(14)	0.0364(13)	0.0537(17)	−0.0123(12)	−0.0062(12)	−0.0023(11)
C(1)	0.1955(4)	0.1958(4)	0.8084(4)	0.0392(17)	0.0350(17)	0.0439(20)	−0.0100(15)	−0.0038(15)	−0.0096(14)
N(2)	0.0815(4)	0.2922(4)	0.8166(4)	0.0495(18)	0.0432(18)	0.0454(19)	−0.0046(15)	−0.0030(15)	0.0010(14)
C(3)	−0.0054(5)	0.2859(5)	0.9275(4)	0.0495(22)	0.0455(22)	0.0475(23)	−0.0071(18)	−0.0030(18)	0.0040(17)
N(4)	0.0150(4)	0.1924(4)	1.0195(4)	0.0456(18)	0.0526(20)	0.0451(20)	−0.0057(16)	−0.0040(15)	0.0023(15)
C(5)	0.1348(4)	0.1012(4)	0.9981(4)	0.0422(19)	0.0468(21)	0.0431(21)	−0.0069(17)	−0.0101(16)	−0.0056(15)
N(6)	0.2324(4)	0.0989(4)	0.8910(3)	0.0411(16)	0.0463(18)	0.0411(17)	−0.0089(15)	−0.0079(13)	−0.0028(13)
N(7)	−0.1217(6)	0.3835(5)	0.9436(4)	0.0736(29)	0.0663(28)	0.0528(25)	0.0006(21)	0.0051(21)	0.0302(23)
C(8)	−0.1603(10)	0.4839(8)	0.8468(6)	0.1170(57)	0.0815(45)	0.0647(38)	−0.0071(33)	−0.0113(38)	0.0471(42)
C(9)	−0.2075(11)	0.6135(8)	0.8719(7)	0.1245(64)	0.0713(42)	0.0832(49)	−0.0066(37)	−0.0086(45)	0.0282(42)
C(10)	−0.3230(9)	0.6199(8)	0.9888(7)	0.0972(48)	0.0736(40)	0.0918(50)	−0.0329(38)	−0.0213(40)	0.0286(36)
C(11)	−0.2817(11)	0.5094(9)	1.0848(7)	0.1317(69)	0.1053(60)	0.0711(44)	−0.0383(43)	−0.0099(45)	0.0358(52)
C(12)	−0.2309(8)	0.3814(8)	1.0583(6)	0.0820(41)	0.0958(50)	0.0596(35)	−0.0026(34)	0.0131(31)	0.0298(36)
N(13)	0.1618(4)	0.0072(4)	1.0874(4)	0.0555(21)	0.0580(22)	0.0410(19)	−0.0048(17)	−0.0088(16)	0.0089(17)
C(14)	0.0643(5)	−0.0026(6)	1.2059(4)	0.0510(23)	0.0650(29)	0.0445(24)	−0.0012(21)	−0.0049(19)	−0.0009(20)
C(15)	0.1430(7)	−0.0080(7)	1.2899(5)	0.0843(38)	0.0775(37)	0.0519(29)	−0.0148(27)	−0.0128(27)	−0.0143(29)
C(16)	0.2735(7)	−0.1194(9)	1.2821(6)	0.0717(36)	0.1280(62)	0.0563(33)	−0.0103(36)	−0.0268(29)	0.0051(37)
C(17)	0.3683(7)	−0.1077(9)	1.1585(6)	0.0518(29)	0.1215(59)	0.0776(42)	−0.0087(40)	−0.0212(28)	0.0062(32)
C(18)	0.2866(6)	−0.1000(6)	1.0754(5)	0.0669(30)	0.0610(29)	0.0535(27)	−0.0123(23)	−0.0142(23)	0.0184(23)
C(19)	0.1278(9)	0.3241(7)	0.5408(8)	0.1000(47)	0.0616(33)	0.1127(56)	−0.0197(35)	−0.0686(45)	0.0097(31)
C(20)	0.0681(15)	0.3017(12)	0.4661(12)	0.2117(125)	0.1335(88)	0.1690(109)	−0.0451(81)	−0.1465(106)	0.0484(86)
C(21)	0.3841(6)	−0.0566(5)	0.6717(6)	0.0674(29)	0.0391(21)	0.0802(36)	−0.0196(23)	−0.0187(26)	−0.0064(19)
C(22)	0.4996(8)	−0.1627(5)	0.7048(7)	0.0923(41)	0.0418(25)	0.0952(47)	−0.0181(28)	−0.0317(36)	0.0056(25)
N(23)	0.7502(4)	0.3142(4)	0.3914(4)	0.0484(19)	0.0519(21)	0.0607(24)	−0.0243(18)	−0.0093(17)	0.0020(15)
O(5)	0.6384(4)	0.2766(3)	0.4633(4)	0.0628(19)	0.0404(16)	0.0694(23)	−0.0201(15)	−0.0010(17)	−0.0033(13)
O(6)	0.7502(4)	0.4367(4)	0.3711(4)	0.0537(18)	0.0482(18)	0.0747(24)	−0.0158(17)	0.0088(16)	−0.0074(14)
O(7)	0.8509(5)	0.2381(5)	0.3443(5)	0.0660(23)	0.0748(27)	0.1157(39)	−0.0547(28)	−0.0001(24)	0.0101(20)

[a] The anisotropic temperature factor exponent takes the form: $-2(\pi)^2[U(11)ha^{*2} + U(22)kb^{*2} + U(33)lc^{*2} + 2(U(23)kb^*lc^* + U(13)ha^*lc^* + U(12)ha^*kb^*)]$.

TABLE V. Structural Parameters for $UO_2(NO_3)_2\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}_2$

Bond lengths (Å)			
U(1)–O(4)	1.764(5)	U(1)–O(1)	2.381(3)
U(1)–O(5)	2.506(3)	U(1)–O(6)	2.523(3)
U(1)–O(4a)	1.764(5)	U(1)–O(1a)	2.381(3)
U(1)–O(5a)	2.506(3)	U(1)–O(6a)	2.523(3)
P–O(1)	1.472(4)	P–O(2)	1.554(5)
P–O(3)	1.546(3)	P–C(1)	1.817(4)
O(2)–C(19)	1.466(8)	O(3)–C(21)	1.459(7)
C(1)–N(2)	1.326(5)	C(1)–N(6)	1.318(5)
N(2)–C(3)	1.356(6)	C(3)–N(4)	1.331(6)
C(3)–N(7)	1.350(6)	N(4)–C(5)	1.340(5)
C(5)–N(6)	1.366(5)	C(5)–N(13)	1.328(6)
N(7)–C(8)	1.463(9)	N(7)–C(12)	1.478(8)
C(8)–C(9)	1.424(12)	C(9)–C(10)	1.532(11)
C(10)–C(11)	1.515(12)	C(11)–C(12)	1.415(13)
N(13)–C(14)	1.463(6)	N(13)–C(18)	1.462(7)
C(14)–C(15)	1.492(10)	C(15)–C(16)	1.524(10)
C(16)–C(17)	1.503(9)	C(17)–C(18)	1.498(11)
C(19)–C(20)	1.362(21)	C(21)–C(22)	1.481(8)
N(23)–O(5)	1.255(5)	N(23)–O(6)	1.256(6)
N(23)–O(7)	1.212(6)		
Bond angles (°)			
O(4)–U(1)–O(1)	91.7(2)	O(4)–U(1)–O(5)	87.1(2)
O(1)–U(1)–O(5)	65.7(1)	O(4)–U(1)–O(6)	92.5(2)
O(1)–U(1)–O(6)	115.1(1)	O(5)–U(1)–O(6)	49.9(1)
O(4)–U(1)–O(4a)	180.0	O(1)–U(1)–O(4a)	88.3(2)
O(5)–U(1)–O(4a)	92.9(2)	O(6)–U(1)–O(4a)	87.5(2)
O(4)–U(1)–O(1a)	88.3(2)	O(1)–U(1)–O(1a)	180.0
O(5)–U(1)–O(1a)	114.3(1)	O(6)–U(1)–O(1a)	64.9(1)
O(4a)–U(1)–O(1a)	91.7(2)	O(4)–U(1)–O(5a)	92.9(2)
O(1)–U(1)–O(5a)	114.3(1)	O(5)–U(1)–O(5a)	180.0
O(6)–U(1)–O(5a)	130.1(1)	O(4a)–U(1)–O(5a)	87.1(2)
O(1a)–U(1)–O(5a)	65.7(1)	O(4)–U(1)–O(6a)	87.5(2)
O(1)–U(1)–O(6a)	64.9(1)	O(5)–U(1)–O(6a)	130.1(1)
O(6)–U(1)–O(6a)	180.0	O(4a)–U(1)–O(6a)	92.5(2)
O(1a)–U(1)–O(6a)	115.1(1)	O(5a)–U(1)–O(6a)	49.9(1)
O(1)–P–O(2)	115.2(2)	O(1)–P–O(3)	111.0(2)
O(2)–P–O(3)	104.8(2)	O(1)–P–C(1)	110.4(2)
O(2)–P–C(1)	106.4(2)	O(3)–P–C(1)	108.7(2)
U(1)–O(1)–P	158.8(3)	P–O(2)–C(19)	122.9(5)
P–O(3)–C(21)	123.8(3)	P–C(1)–N(2)	113.4(3)
P–C(1)–N(6)	117.5(3)	N(2)–C(1)–N(6)	129.1(4)
C(1)–N(2)–C(3)	112.6(4)	N(2)–C(3)–N(4)	125.4(4)
N(2)–C(3)–N(7)	116.1(4)	N(4)–C(3)–N(7)	118.5(4)
C(3)–N(4)–C(5)	115.4(4)	N(4)–C(5)–N(6)	124.6(4)
N(4)–C(5)–N(13)	117.9(4)	N(6)–C(5)–N(13)	117.5(4)
C(1)–N(6)–C(5)	112.8(3)	C(3)–N(7)–C(8)	122.6(5)
C(3)–N(7)–C(12)	121.2(5)	C(8)–N(7)–C(12)	115.5(5)
N(7)–C(8)–C(9)	112.5(8)	C(8)–C(9)–C(10)	114.2(7)
C(9)–C(10)–C(11)	110.6(6)	C(10)–C(11)–C(12)	116.0(8)
N(7)–C(12)–C(11)	112.2(6)	C(5)–N(13)–C(14)	122.7(4)
C(5)–N(13)–C(18)	123.3(4)	C(14)–N(13)–C(18)	113.9(4)
N(13)–C(14)–C(15)	110.5(5)	C(14)–C(15)–C(16)	111.8(6)
C(15)–C(16)–C(17)	110.3(6)	C(16)–C(17)–C(18)	111.9(6)
N(13)–C(18)–C(17)	110.9(6)	O(2)–C(19)–C(20)	111.5(8)
O(3)–C(21)–C(22)	108.1(6)	O(5)–N(23)–O(6)	115.3(4)
O(5)–N(23)–O(7)	122.5(5)	O(6)–N(23)–O(7)	122.2(4)
U(1)–O(5)–N(23)	97.9(3)	U(1)–O(6)–N(23)	96.9(2)

the mass spectrum. The infrared spectrum shows several strong diagnostic absorptions; the phosphoryl stretch, the C–N ring stretch and the POC stretch appear at 1227, 1551 and 979 cm^{-1}, respectively. The phosphoryl stretch is down frequency from the ν_{PO} bands in $(EtO)_3PO$ [9] 1260 cm^{-1}, $(EtO)_2(Ph)PO$ [10] 1257 cm^{-1} and $(i\text{-}PrO)_2(Ph)PO$ [9] 1253 cm^{-1}. The displacement of ν_{PO} in **1**, relative to the absorption in these phosphates and phosphonates, suggests that the triazine acts as a good electron releasing substituent. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a singlet at δ 6.0, and this resonance is upfield of the resonance for $(EtO)_2(Ph)PO$ [11] δ 16.9 and $(i\text{-}PrO)_2(Ph)PO$ [9] δ 15.7. The trend in these data is also consistent with the triazine ring acting as an electron releasing substituent relative to a phenyl group. The ^1H and $^{13}C\{^1H\}$ NMR data have been obtained, and assignments are consistent with the proposed structure of **1**.

The ligand **1**, in combination with $UO_2(NO_3)_2$, forms a pale yellow crystalline complex. Elemental analyses are consistent with the formation of a 2:1 complex (**2**) $UO_2(NO_3)_2\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}_2$. The infrared spectrum of the complex shows a phosphoryl stretching frequency at 1193 cm^{-1}. The coordination shift, $\Delta\nu_{PO} = 34$ cm^{-1}, is relatively small, and it may be compared with coordination shifts in several other uranyl–phosphoryl complexes: $UO_2(NO_3)_2L_2$, L = $(EtO)_3PO$ [9] 75 cm^{-1}, $(i\text{-}PrO)_2(Ph)PO$ [9] 68 cm^{-1}; $UO_2(NO_3)_2L$, L = $(EtO)_2P(O)CH_2C(O)NEt_2$ [12] 61 cm^{-1}, $(EtO)(Ph)P(O)CH_2C(O)NEt_2$ [12] 56 cm^{-1} and $Ph_2P(O)pyO$ [12] 42 cm^{-1}. The coordination shift for **2** is unexpectedly small given the anticipitated electron releasing character of the triazine ring and expected higher base strength of the phosphoryl oxygen atom in **1**. On the other hand, the asymmetric uranyl stretch in **2** occurs at 933 cm^{-1}. This frequency is intermediate in a range of ν_{UO_2} stretches (950–900 cm^{-1}) [12, 13] for a number of uranyl–phosphoryl complexes, and these data suggest an intermediate base strength for **1**.

The crystal and molecular structures of the ligand **1** and uranyl complex **2** were determined in order to explore potential steric and electronic effects which might influence the coordination ability of the triazine phosphonate prior to incorporation in a polymer. A view of the ligand is shown in Fig. 1, and a view of the complex is given in Fig. 2. The structure of the ligand shows a central, planar C_3N_3 triazine ring with piperidino substituents at C(3) and C(5) and a diethoxy phosphoryl fragment at C(1). The triazine ring is irregular with C–N bond distances spanning a range 1.361(3) Å to 1.319(3) Å with an average distance, 1.343(3) Å. The two longer distances involve C(3)–N(2) and C(5)–N(6) while the shorter distances involve the phosphoryl bonded carbon atom, C(1)–N(2) and C(1)–N(6).

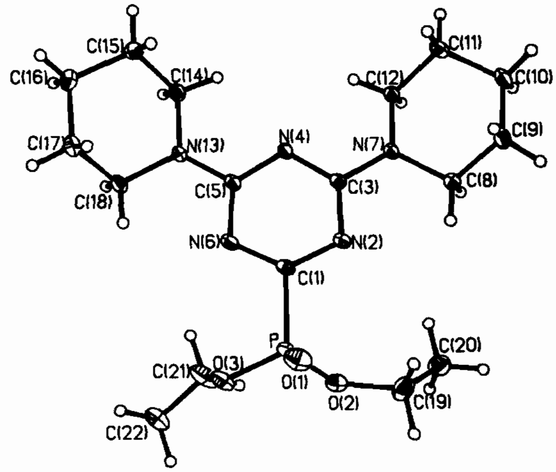

Fig. 1. Molecular geometry and atom labeling scheme for $\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}$ (25% thermal ellipsoids).

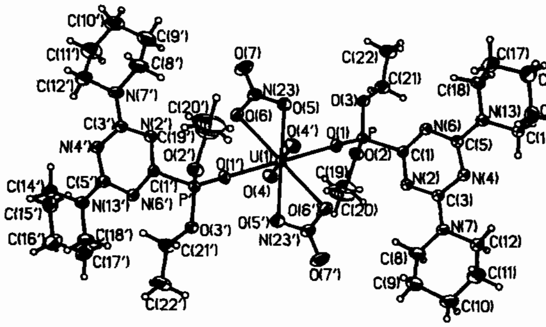

Fig. 2. Molecular geometry and atom labeling scheme for $UO_2(NO_3)_2\{C_3N_3(C_5H_{10}N)_2[(EtO)_2P(O)]\}$ (25% thermal ellipsoids.

The sums of the bond angles about C(1), C(3) and C(5) are 360°. The piperidino rings have a chair conformation with C–N bond distances between the piperidino group and the triazine being C(5)–N(13) 1.344(3) Å and C(3)–N(7) 1.358(2) Å. These distances and the planar geometry about N(7) and N(13) suggest some π overlap between the piperidino nitrogen atom and the triazine ring. The phosphoryl phosphorus atom is tetrahedral with the P=O bond vector nearly perpendicular to the C_3N_3 ring (torsion angle O(1)–P–C(1)–N(2) 78.6°). The P=O bond distance P–O(1), 1.452(2) Å, falls within a range, 1.38–1.56 Å (avg. 1.46 Å) for tetrahedral phosphates [14]. The average EtO–P distance, 1.573(2) Å, also falls in a range, 1.56–1.64 Å (avg. 1.59 Å) found in other phosphonates [14].

The structure determination for the complex **2** confirms the 2:1 ligand/UO_2^{2+} stoichiometry. The uranyl ion is linear and bonded to two bidentate nitrate ions and two *trans* phosphoryl oxygen atoms. The structure is centrosymmetric, and there are no intramolecular distortions caused by interactions between the two bulky phosphonate ligands. The uranyl ion U–O(4) distance, 1.764(5) Å, is slightly longer than encountered in a few other uranyl complexes [12–17], e.g., $UO_2(NO_3)_2[(C_4H_9)_3PO]_2$ 1.742(7) Å, $UO_2(Et_2NCS_2)(Ph_3PO)$ 1.70(3) Å, and $UO_2(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$ 1.742(6) Å; however, the distance is very similar to the majority of distances in uranyl–phosphoryl complexes [12–21]. The U–O(1) (phosphoryl) distance in **2**, 2.381(3) Å, is similar to the distance in $UO_2(MeCO_2)_2(Ph_3PO)_2$ 2.37(3) Å and in $UO_2(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$ 2.377(4) Å, where the two donor sites are in a *cis* orientation, but longer than the distance in $UO_2(NO_3)_2[(C_4H_9)_3PO]_2$, 2.347(6) Å. Based upon coordinate bond distance comparisons from a rather large number of uranyl–phosphoryl structures [12–21], it may be concluded that ligand **1** acts as an intermediate strength phosphoryl donor toward $UO_2(NO_3)_2$.

The P=O distance in **2**, P–O(1) 1.472(4) Å, is also within the range (1.49–1.45 Å) of distances reported earlier [12–21] and the distance is significantly longer than the P=O distance in the free ligand **1**. The P–C(1) distance in **2**, 1.817(4) Å, is shorter than that in **1**, 1.834(2) Å, which is consistent with the expected electron demand in the ligand backbone upon coordination. There are no significant changes in the parameters in the triazine or piperidino fragments in **2**.

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