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Steric effects in complexes of diphenyl(2-pyridyl)phosphine oxide with the uranyl ion. Synthetic, structural and theoretical studies

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ABSTRACT

Uranyl complexes containing diphenyl(2-pyridyl)phosphine oxide, with the formulae $[UO_2(NO_3)_2(\{C_6H_5\}_2POC_5H_4N)_2]$ (**1**) and $[UO_2(DBM)_2(\{C_6H_5\}_2POC_5H_4N)]$ (**2**) (where DBM = $C_6H_5COCHCOC_6H_5$), were prepared and characterized by IR, NMR spectroscopic and elemental analysis methods. The structures of the compounds were determined by X-ray diffraction methods and revealed a monodentate mode of bonding for the ligand through the phosphine oxide oxygen atom to the uranyl group. The pyridyl nitrogen atom of the ligand is uncoordinated. The uranyl group is surrounded by eight oxygen atoms in a hexagonal bi-pyramidal geometry in **1** and seven oxygen atoms in a pentagonal bi-pyramidal geometry in **2**.

1. Introduction

In recent years the structural and coordination chemistry of uranium has grown in interest due to the availability of new synthetic strategies [1] and also interesting properties such as, selective ion-exchange, mixed valencies, ionic conductivity, enhanced fluorescence, magnetic ordering and non-linear optical properties exhibited by its complexes [2]. A basic understanding of the complex chemistry of the uranyl ion is very important in facilitating the design of new ligands for the selective separation of this ion from irradiated nuclear fuel, seawater, nuclear plant effluents, biological and environmental samples [3–5]. Many multifunctional phosphine oxide based ligands have been examined for their ability to separate actinides and lanthanides from high level nuclear waste solutions [6] and their structures with actinide and lanthanide ions have also been reported [7]. The chemistry of mono and bi functional phosphine oxides with the uranyl ion is well documented. In all cases the phosphine oxide bonds through the oxygen atom to the uranyl ion [8]. The chemistry of bi-functional phosphine oxides with the uranyl ion shows different modes of bonding for the ligand depending upon the stoichiometry and nature of other groups present in the metal coordination sphere [8c]. We are interested in the coordination and structural chemistry of bi-functional ligands containing soft nitrogen and hard oxygen donor atoms with uranyl and lanthanide ions [9]. Our recent studies support [9c] the earlier observations that ligands forming five membered metallocyclic rings with the metal ion are more subject to steric control than corresponding ligands forming six membered rings [10]. Diphenyl(2-pyridyl)phosphine oxide is a bi-functional ligand having soft pyridine nitrogen and hard phosphine oxide groups. The chemistry of this ligand with transition metal ions is well reported [11] and it is found to act as either a monodentate ligand, bonding via the phosphine oxide oxygen atom, or as a bidentate chelating ligand, bonding via both the phosphine oxide oxygen and pyridyl nitrogen atoms. However, no report on the chemistry of this ligand with any of the 4f or 5f elements is available in the literature to our knowledge. In continuation of our interest in the chemistry of phosphine oxide with the uranyl ion [8c,d,12a,b], we report herein the complex chemistry of diphenyl(2-pyridyl)phosphine oxide with uranyl nitrate and uranyl bis(β-dibenzoylmethanate) and have explained the stability of the complex formed by using theoretical studies.

2. Materials and methods

2.1. General considerations

All reagents and solvents were of analytical grade and used as received. IR spectra were recorded as Nujol mulls using a JASCO-610 FITR spectrometer. ^1H and ^{31}P NMR spectra were recorded using a Bruker AMX-300 spectrometer. The chemical shifts (δ)

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are reported in ppm. Electrospray ionization mass spectrometric detection of positive ions in CH_2Cl_2 or CH_3COCH_3 was recorded using a MicrOTOF Q-II instrument. The samples were introduced into the source with a syringe pump. Nitrogen was employed as both the drying and spraying gas with a source temperature of 180 °C. The cone voltage was set to 45 V, the voltage applied on the capillary was 1162 kV and the sample solution flow rate was 5 μL min^{-1}. The spectra were recorded for *m*/*z* values of 100–1000.

2.2. Synthesis of **L**

To a solution of diphenyl, 2-pyridyl phosphine (5 g, 19 mmol) in benzene (50 mL), 30% H_2O_2 (2 mL) was added and stirred for 5 h. This solution was dried over anhydrous sodium sulfate and filtered. The filtrate on evaporation yielded a light yellow colored powder, which was filtered, washed with hexane and dried (Yield. 85 %). $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$) δ (ppm): 21.280. IR (cm^{-1}) ν: 1191 (P=O). Anal. Calc. for $C_{17}H_{14}NPO$: C, 73.1; H, 5.0; N, 5.0. Found: C, 72.8; H, 4.8; N, 4.8%.

2.3. Synthesis of **1**

To a solution of L (112 mg, 400 mmol) in methanol (20 mL), solid $[UO_2(NO_3)_2{\cdot}6H_2O]$ (100 mg, 200 mmol) was added and stirred for few minutes until all the solid dissolved to give a clear solution. This solution was filtered and allowed to evaporate slowly at room temperature. This process yielded a yellow crystalline solid, which was filtered, washed with hexane and dried (yield 84 %). $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$) δ (ppm): 36.726. IR (cm^{-1}) ν: 1161 (P=O). Anal. Calc. for $C_{34}H_{28}N_4P_2O_{10}U$: C, 42.9; H, 2.9; N, 5.9. Found: C, 42.6; H, 2.8; N, 5.6%.

2.4. Synthesis of **2**

To a solution of L (57 mg, 200 mmol) in methylene chloride (20 mL), solid $[UO_2(DBM)_2{\cdot}H_2O]$ (150 mg, 200 mmol) was added and stirred for few minutes until all the solid dissolved to give a clear solution. This solution was filtered and layered with iso-octane. The solution on slow evaporation yielded an orange colored crystalline solid, which was filtered, washed with hexane and dried (yield 90 %). $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$) δ (ppm): 31.796. IR (cm^{-1}) ν: 1171 (P=O). Anal. Calc. for $C_{47}H_{36}NPO_7U$: C, 56.7; H, 3.6; N, 1.4. Found: C, 56.6; H, 3.7; N, 1.2%.

2.5. Theoretical methods

Geometry optimization for the diphenyl(2pyridyl)phosphine oxide ligand and complex **1** has been carried out by applying a popular non-local correlated hybrid density functional, namely, B3LYP. Gaussian type atomic basis functions, 6-31+G(d), were adopted for the H, C, N and O atoms and for U atom very recently suggested basis sets, SARC-ZORA [13a], were used for all the calculations. SARC-ZORA basis sets are segmented all-electron scalar relativistic basis sets in which the coefficients of contracted GTOs have been optimized for use with the ZORA scalar relativistic Hamiltonian. These particular basis sets for U were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Pacific Northwest National Laboratory [13b]. The quasi-Newton–Raphson based algorithm has been applied to carry out geometry optimization to locate the minimum energy structure in each case. Hessian calculations have also been carried out to check the nature of the equilibrium geometry. A macroscopic solvation effect of the solvent dichloromethane has been incorporated in the energy calculation through the polarizable continuum model (PCM). All these calculations have been carried out with the GAMESS suite of *ab initio* programs [13c].

2.6. Crystal structure determinations

Crystal data for **1** and **2** were measured on an Oxford Diffraction X-Calibur CCD system at 150(2) K with Mo Kα radiation (λ = 0.71073 Å). The crystals were positioned 50 mm from the CCD. 321 Frames were measured with a counting time of 10 s. Data analyses were carried out with the CrysAlis program [14a]. The structures were solved using direct methods with the shelxs97 program [14b]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to carbon atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they are attached. Empirical absorption corrections were carried out using the abspack program [14c]. The structures were refined to convergence on F^2 using shelxl97 [14b]. In the structure of **1**, the nitrogen atom of the pyridyl ring was disordered over two positions with a refined ratio of 62:38. In the structure of **2**, four of the aromatic rings showed severe disorder and in each case two orientations were included in the refinement with occupation factors x and $1 - x$, with x refining to values close to 0.5. Selected crystallographic data for **1** and **2** are summarized in Table 1.

3. Results and discussion

3.1. Synthesis of the diphenyl(2-pyridyl)phosphine oxide ligand (**L**)

This ligand was prepared by the oxidation of the corresponding phosphine with H_2O_2 in benzene. The IR spectrum shows the presence of a P=O group (1191 cm^{-1}) in the synthesized ligand. The ^{31}P NMR spectrum shows a single resonance at δ = 21.28 ppm, which is ca. 25.18 ppm downfield compared to that of the starting phosphine (δ = −3.90 ppm). The CHN analyses support the expected stoichiometry for the newly prepared ligand.

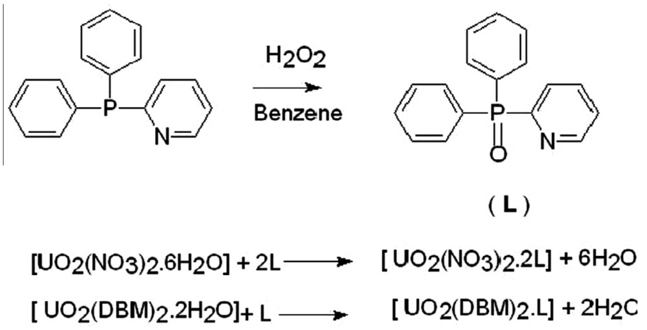
3.2. Synthesis of the diphenyl(2-pyridyl)phosphine oxide, uranyl nitrate complex (**1**)

The reaction of $[UO_2(NO_3)_2{\cdot}6H_2O]$ with the ligand $\{C_6H_5\}_2POC_5H_4N$ in methanol yielded compound **1** (Scheme 1). The CHN analyses revealed that the ratio of uranyl nitrate to ligand is 1:2. The IR spectrum of **1** shows that the water molecules from the starting compound $[UO_2(NO_3)_2{\cdot}6H_2O]$ are completely replaced by the ligand and that the ligand is bonded through the phosphoryl oxygen atom to the uranyl group. The observed frequency difference for the PO group ($\Delta\nu_{PO}$ = 30 cm^{-1}, where $\Delta\nu_{PO} = \nu_{PO\ (free\ ligand)} - \nu_{PO(coordinated)}$)

Table 1
Crystal data refinement of compounds **1** and **2**.

	1	**2**
Empirical formula	$C_{34}H_{28}N_4O_{10}\ P_2U$	$C_{47}H_{36}NO_7PU$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	9.726(3)	17.9927(6)
b (Å)	11.074(3)	11.1401(3)
c (Å)	15.9365(14)	20.5688(6)
β (°)	93.180(19)	101.982(3)
V (cm^3)	1713.9(7)	4033.0(2)
Z	2	4
ρ_{calc} (g cm^{-3})	1.846	1.640
μ (mm^{-1})	4.893	4.118
Reflections collected/unique	4935/3357	8732/6817
Data/restraints/parameters	3357/0/233	6817/0/398
Goodness of fit (GOF) on F^2	1.011	1.180
Final R_1 indices [$I > 2\sigma(I)$]	0.0606	0.0695
wR_2 indices (all data)	0.1080	0.1300

$w = 1/[\sigma^2(F_o^2) + (0.0062P)^2 + 0.000P]$ for **1**, $w = 1/[\sigma^2(F_o^2) + (0.0176P)^2 + 24.1300P]$ for **2**, where $P = (F_o^2 + 2F_c^2)/3$.



Scheme 1. Synthesis of the ligands and its uranyl complexes.

shows that the phosphoryl oxygen atom is bonded to the uranyl ion directly [8b–e,12a–b]. This difference is comparable in magnitude with those observed in $[UO_2(NO_3)_2(DPPMO_2)]$ (DPPMO = bis(diphenylphosphino)methane dioxide) [8c], $[UO_2(NO_3)_2(DPPFO_2)]$ (DPPFO = 1,1′-bis(diphenylphosphino)ferrocene dioxide) [8d], $[UO_2Cl_2(DPPFO_2)]$ [8e], $[UO_2(DPPMO_2)_2(OPPh_3)](BF_4)_2$ [12a] and $[UO_2(OPPh_3)_4](OTf)_2$ [12b]. The ^{31}P NMR spectrum of **1** shows a single resonance at δ 36.73 ppm, which is ca. 15.45 ppm downfield compared to that of the free ligand. This observation provides further evidence that the phosphoryl oxygen atom is coordinated to the uranyl ion. The ESI-MS spectrum of **1** in acetonitrile shows the presence of peaks at *m*/*z* of 581.5 $[(UO_2L_3(H_2O)_3+2H)^{2+}$, 100%] and 302 $[(UO_2L(H_2O)_3+H)^{2+}$, 100%], indicating that the metal ligand bond is retained in solution. It is apparent from the IR, NMR spectral and CNH analysis results that the ligand acts as a monodentate ligand and bonds through the phosphoryl oxygen atom to the uranyl ion. The structure of **1** has been determined by single crystal X-ray diffraction methods and confirms the spectral and analysis results.

3.3. Structure of $[UO_2(NO_3)_2(\{C_6H_5\}_2POC_5H_4N)_2]$ (1)

The structure of **1** is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The structure consists of a centrosymmetric $[UO_2(NO_3)_2(\{C_6H_5\}_2POC_5H_4N)_2]$ moiety, in which the uranium atom is surrounded by eight oxygen atoms in a hexagonal bi-pyramidal geometry. Four oxygen atoms of the two bidentate nitrate groups, together with two oxygen atoms of two diphenyl(2-pyridyl)phosphine oxide ligands form the equatorial hexagonal plane. The UO_6 atoms in the equatorial plane show an r.m.s deviation of 0.029 Å. The two uranyl oxygen atoms occupy the axial positions.

This type of coordination is similar to that observed in phosphine oxide, amide, pyrolidone compounds with uranyl nitrate, such as $[UO_2(NO_3)_2(OPPh_3)_2]$ [8], $[UO_2(NO_3)_2(amide)_2]$ [15a], $[UO_2(NO_3)_2$(N-cyclohexyl,2-pyrrolidone)$_2]$ [15b] and $[UO_2(NO_3)_2$(1,3-dimethyl,2-imidazolidone)$_2]$ [15c]. The average U–O$_{(\text{phosphine oxide})}$ distance (2.350(4) Å) in **1** is comparable in magnitude with those of earlier reported uranyl nitrate-phosphine compounds, such as $[UO_2(NO_3)(TBPO)_2]$ (TBPO = tributyl phosphine oxide) [8a], $[UO_2(NO_3)_2(DPEPA)_2]$ (2.347(5), 2.379(4) Å) (DPEPA = diphenyl-N,N-ethylphosphine amide) [8b], $[UO_2(NO_3)_2(TPPA)_2]$ (2.340(3) Å) (TPPA = tripiperidine phosphine oxide) [8b], $[UO_2(NO_3)_2(DPPMO_2)]$ (2.386(9) Å) [8c], $[UO_2(NO_3)_2(CMPO)]$ (CMPO = carbamoylmethyl phosphine oxide) (2.38(2) Å) [7c], $[UO_2(NO_3)_2(DPPFO_2)]$ (2.352(2) Å) [8d], $[UO_2(DPPMO_2)_2(OPPh_3)]$ (2.343(2) Å) [12a] and $[UO_2(OPPh_3)_4]^{2+}$ (2.2907–2.3034(17) Å) [12b–c]. The observed average U–O(NO_3) (2.534(5) Å) [8,12] and U–O(uranyl) (1.758(4) Å) [8,12,15,16] distances are normal. The angles subtended at the metal atom show that the uranium atom has a slightly distorted hexagonal bi-pyramidal geometry.

It is interesting to note here that the ligand forms a 2:1 complex with uranyl nitrate and bonds through the phosphine oxide oxygen atoms to the metal center, leaving the pyridyl nitrogen atom un-coordinated. The chelating mode of bonding via the phosphine oxide oxygen and pyridyl nitrogen atoms is found for this ligand with transition metal ions, forming a five membered metallocyclic ring. We have also reported recently that the pyrazolyl urea ligand [9] forms a five member metallocyclic ring with the uranyl ion via the pyrazolyl nitrogen and carbamoyl oxygen atoms. In order to find out the reason for not forming the five membered metallocyclic ring or not acting as a chelating ligand with the uranyl ion, theoretical studies were carried out. Theoretical studies (see below) clearly reveal that steric effects play an important role in deciding the mode of bonding for this ligand.

3.4. The diphenyl(2-pyridyl)phosphine oxide uranyl bis(dibenzoylmethanate) complex (2)

The reaction of $(C_6H_5)_2POC_5H_4N$ with $[UO_2(C_6H_5COCHCOC_6H_5)_2{\cdot}2H_2O]$ yielded compound **2** (Scheme 1). The CHN analyses

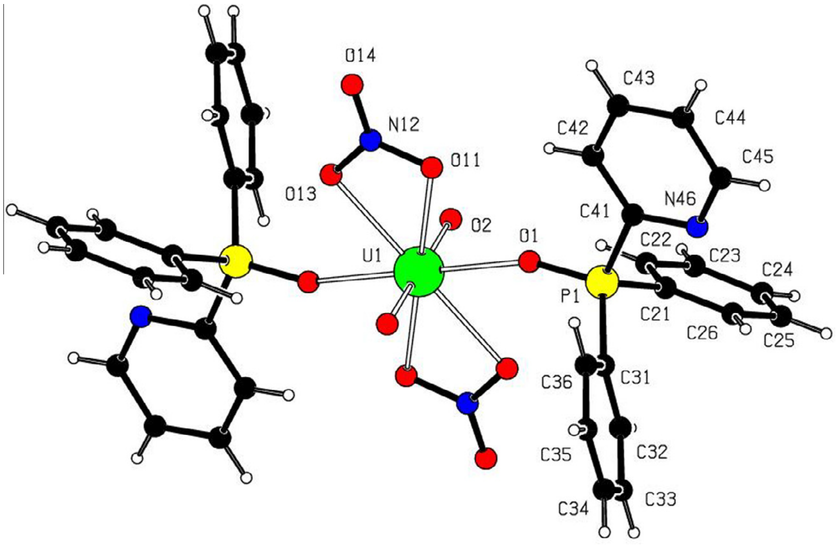


Fig. 1. The centrosymmetric structure of **1**. The nitrogen atom is disordered over two sites N46 and C26 with occupation factors of 0.62 and 0.38 respectively.

revealed that the ratio of ligand to uranyl bis(dibenzoylmethanate) is 1:1. The IR spectrum shows that the water molecules from the starting compound [$UO_2(C_6H_5COCHCOC_6H_5)_2{\cdot}2H_2O$] are completely replaced by the ligand and furthermore the observed frequency difference for the phosphoryl group ($\Delta\nu_{PO} = 20\ cm^{-1}$, where $\Delta\nu_{PO} = \nu_{PO(free\ ligand)} - \nu_{PO(coordinated)}$) is consistent with the supposition that the phosphoryl group is bonded to the uranyl ion directly.

The ^{31}P NMR spectrum of **2** shows a single resonance at 31.79 ppm, which is deshielded about ca 10.51 ppm with respect to the free ligand, indicating that the metal ligand bond persists in solution. The structure of **2** has been determined by single crystal X-ray diffraction methods and confirms the spectral and analysis results.

*3.5. Structure of [$UO_2(C_6H_5COCHCOC_6H_5)_2(C_6H_5)_2POC_5H_5N$] (**2**)*

The structure of **2** is shown in Fig. 2 together with the numbering scheme and selected bond distances and angles are given in Table 2. The structure shows that the uranyl ion is bonded to two $C_6H_5COCHCOC_6H_5$ groups and one diphenyl(2-pyridyl) phosphine oxide ligand to give a coordination number of seven. The diphenyl(2-pyridyl)phosphine oxide ligand acts as a monodentate ligand and is bonded through the phosphine oxygen atom to the uranyl ion. Four oxygen atoms from two bidentate $C_6H_5COCHCOC_6H_5$ groups and one oxygen atom from the phosphine oxide ligand form the equatorial plane and together with two oxygen atoms of the uranyl ion form a pentagonal bi-pyramidal geometry around the uranium(VI) ion.

The five oxygen atoms in the equatorial plane show an r.m.s deviation of 0.102 Å. Similar structures are also observed in phosphine oxide, sulfoxide, ketone, N-oxide and amide compounds with uranyl bis(β-diketonates), viz: [$UO_2(DBM)_2(OPPh_3)$] (DBM = dibenzoylmethanide) [17a], [$UO_2(TTA)_2TIBP$] (TTA = theonoyltrifluoroacetate; TIBP = triisobutylphosphate) [17b], [$UO_2(DBM)_2(C_6H_5SOCH_3)$] [17c], [$UO_2(TTA)_2(C_5H_5NO)$][17d], [$UO_2(DBM)_2$(camphor] [17e], [$UO_2(DBM)_2(C_4H_9CON\{C_4H_9)_2)$] [17f] and [$UO_2(DBM)_2(^iC_3H_7CON\{^iC_3H_7)_2$] [15a]. The observed U–O phophine oxide bond distance (2.389(5) Å) is comparable with those of the earlier reported uranyl bis (β-diketonate)-phosphine oxide compounds [17a,b,18]. All other bond distances and angles are normal [17,18].

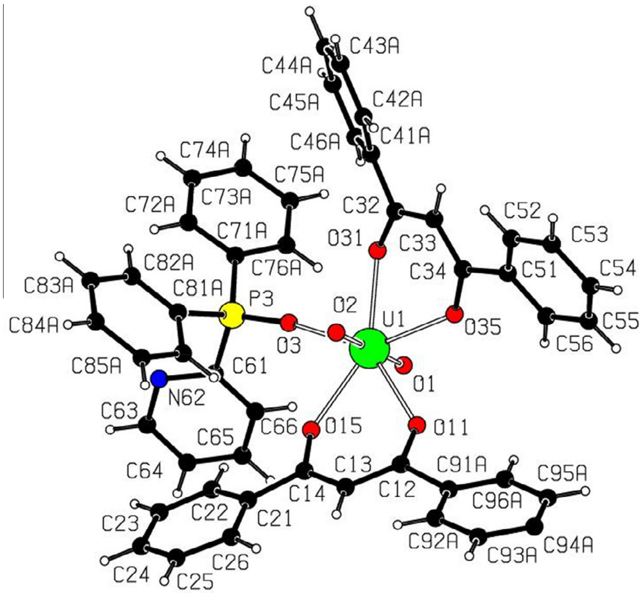


Fig. 2. Structure of **2**. Four of the aromatic rings are disordered over two orientations. Only those with the higher occupancy are shown.

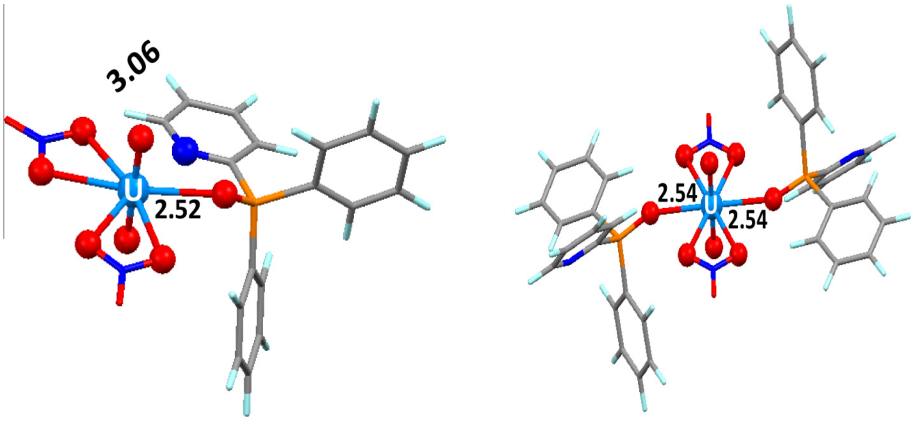
Table 2
Important bond lengths (Å) and angles (°) for **1** and **2**.

1			
U1–O1	2.350(5)	U1–O11	2.530(5)
U1–O2	1.758(4)	U1–O13	2.538(5)
P1–O1	1.521(4)		
		O2–U1–O1	89.7(2)
O2–U1–O11	89.8(2)	O2–U1–O13	90.3(2)
O1–U1–O11	64.5(2)	O1–U1–O13	114.6 (2)
O11–U1–O13	50.1(2)	P12–O1–U1	159.6(3)
2			
U1–O1	1.770(5)	U1–O31	2.357(6)
U1–O2	1.775(5)	U1–O35	2.352(6)
U1–O15	2.381(6)	U1–O11	2.329(5)
U1–O3	2.389(5)	P3–O3	1.487(5)
O1–U1–O2	178.7(2)	O31–U1–O35	70.1(2)
O31–U1–O3	73.9(2)	O3–U1–O15	74.3(2)
O11–U1–O15	69.6(2)	O11–U1–O35	72.9(2)
P3–O3–U1	167.4(3)	O3–U1–O35	143.9(2)
O3–U1–O11	142.9(2)		

3.6. Theoretical studies on complexes of diphenyl(2-pyridyl)phosphine oxide with uranyl nitrate

To examine the feasibility of the binding of diphenyl(2-pyridyl)phosphine oxide with the uranyl ion, either as a chelating ligand binding through both the phosphine oxide and pyridyl nitrogen atoms or as a monodentate ligand binding through phosphine oxide oxygen atom, quantum chemical calculations have been carried out. Full geometry optimization of the possible complexes has been performed in the gas phase as well as in dichloromethane solution following a macroscopic solvation model. The minimum energy structures predicted in solution are presented in Fig. 3(a and b).

In the chelated complex (**3a**), the calculated U–O(phosphoryl) and U–N (pyridyl) bond distances are 2.52 and 3.06 Å, respectively. The large U–N bond distance in **3a** appears to be due to steric hindrance between the pyridine ring and the adjacent nitrate groups. The calculated U–O (phosphoryl) bond length of 2.54 Å in the monodentate structure (**3b**) is slightly longer as compared with that obtained for the bidentate chelating structure (**3a**). Note that these bond distance parameters are about 0.1 Å shorter as compared to those calculated in the gas phase. To calculate the binding energy for the chelating mode of bonding between the ligand and $UO_2(NO_3)_2$, the energy of the whole complex (**3a**) was calculated by increasing the distance between the ligand and the $UO_2(NO_3)_2$ moiety to generate a dissociation curve, and thus the binding energy is calculated as 37.7 kcal/mol. In the case of the 2:1 monodentate complex (**3b**), the dissociation curve is generated by calculating the energy by increasing the distance between the U and O atoms of both the ligands. The total binding energy is thus calculated as 51.2 kcal/mol (for two ligands with the monodentate mode of bonding) and the binding energy per ligand is calculated as 25.6 kcal/mol. As expected, the binding energy calculation clearly revealed that the chelating mode of bonding via the phosphoryl oxygen and pyridyl nitrogen atoms (37.7 kcal/mol) is more stable than that of the monodentate mode of bonding via the phosphoryl oxygen atom (25.6 kcal/mol) by 12.1 kcal/mol. However, between the 2:1 complex (**3b**) with two monodentate ligands (51.2 kcal/mol) and the 1:1 complex (**3a**) with one chelating ligand (37.7 kcal/mol), the former is more stable than that of later by 13.5 kcal/mol. This shows clearly that 2:1 complex with two monodentate ligand is energetically more favorable than that of

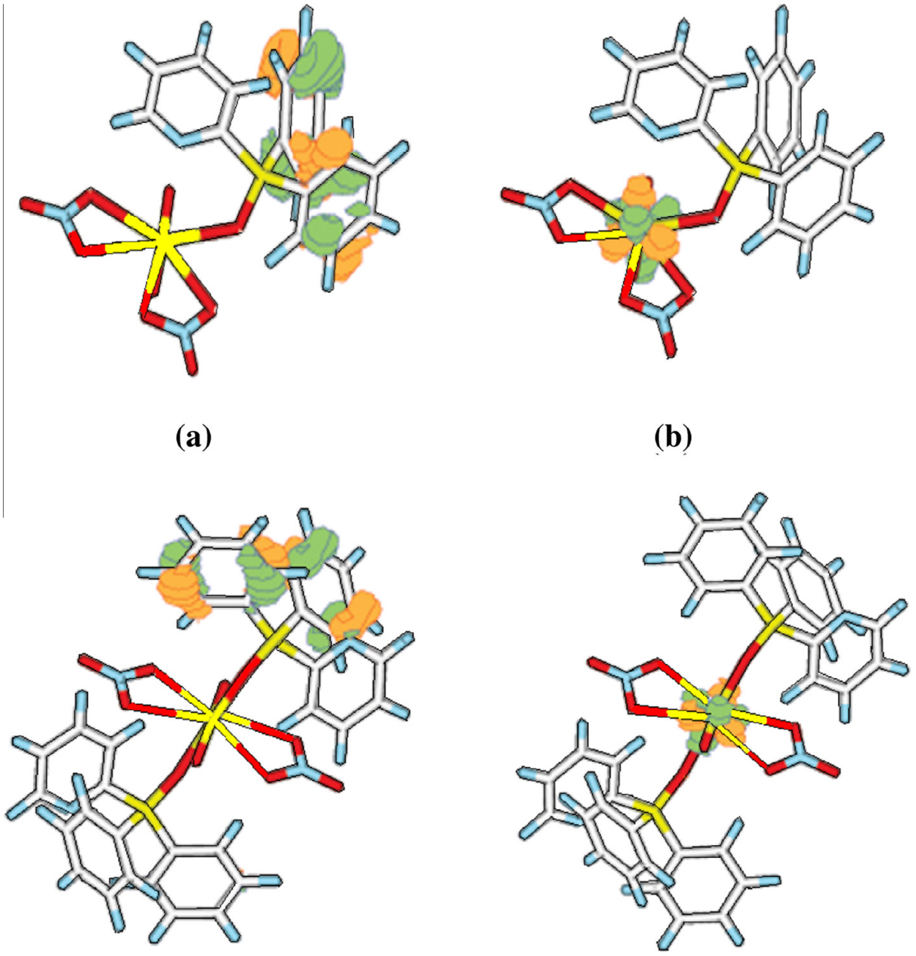


(a) (b)

Fig. 3. (a) Optimized structures for $[UO_2(NO_3)_2L]$ and (b) $[UO_2(NO_3)_2{\cdot}2L]$.

1:1 complex with one chelating ligand. This observation is in agreement with our experimental results.

The HOMOs and LUMOs of the $[UO_2(NO_3)_2L]$ and $[UO_2(NO_3)_2{\cdot}2L]$ complexes are shown in Fig. 4(a–d). It is observed that the basic nature of these orbitals is quite similar in both complexes in that the phenyl π orbitals of the ligand participate in the HOMO, whereas the LUMO is comprised mainly of the $U[5f_{z(x2-y2)}]$ orbital.



(a) (b) (c) (d)

Fig. 4. (a) HOMO of $[UO_2(NO_3)_2L]$, (b) LUMO of $[UO_2(NO_3)_2L]$, (c) HOMO of $[UO_2(NO_3)_2{\cdot}2L]$ and (d) LUMO of $[UO_2(NO_3)_2{\cdot}2L]$.

4. Conclusions

The structural studies on the complexes of diphenyl (2-pyridyl)phosphine oxide with uranyl nitrate and uranyl bis(dibenzoylmethanate) show a monodentate mode of bonding for the ligand. Theoretical studies reveal that the steric effects play an important role in deciding the mode of bonding for the ligand. The 2:1 complex $[UO_2(NO_3)_2{\cdot}2L]$, in which the ligand acts as a monodentate ligand, is energetically more stable by 13.5 kcal/mol than the 1:1 complex $[UO_2(NO_3)_2{\cdot}L]$, in which the ligand acts as a bidentate chelating ligand.

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Appendix A. Supplementary data

CCDC 1025071 and 1025072 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.12.047.

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