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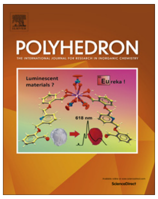

Steric effects in complexes of diphenyl(2-pyridyl)phosphine oxide with the uranyl ion. Synthetic, structural and theoretical studies

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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 $P = (F_o^2 + 2F_c^2)/3$.