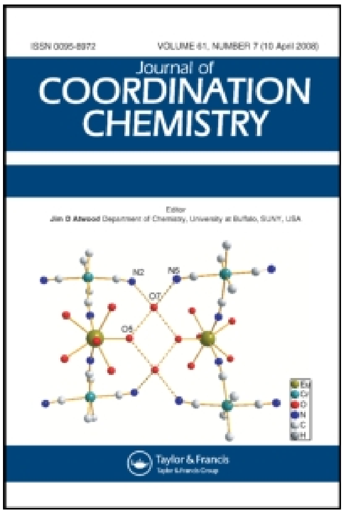

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Bidentate coordination of a diketo phosphorus ylide: synthesis and structure of $[(C_6H_5)_3PC(COCH_3)(COC_6H_5)\text{-}\kappa O,O']UO_2(NO_3)_2$

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Bidentate coordination of a diketo phosphorus ylide: synthesis and structure of $[(C_6H_5)_3PC(COCH_3)(COC_6H_5)\text{-}\kappa O,O']UO_2(NO_3)_2$

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A 1 : 1 chelate complex $[(C_6H_5)_3PC(COCH_3)(COC_6H_5)\text{-}\kappa O,O']UO_2(NO_3)_2$ has been synthesized by reaction of $(C_6H_5)_3PC(COCH_3)(COC_6H_5)$ with $UO_2(NO_3)_2 \cdot 6H_2O$ in methanol at room temperature and characterized by elemental analysis, spectroscopy as well as by single-crystal X-ray diffraction. The complex crystallizes in $P2_1/n$ space group with $a = 10.007(2)$ Å, $b = 15.285(7)$ Å, $c = 19.20(1)$ Å, $\beta = 91.22(3)^\circ$, $V = 2936(2)$ Å^3, $Z = 4$, $D_c = 1.847\,\mathrm{g\,cm^{-3}}$. In the solid state structure, the dihedral angle [88.1(4)°] between the planes defined by the two quartets of atoms O1 O8 O2 O4 and O6 O5 O3 O7 is close to 90°, as expected for a triangulated dodecahedral geometry around uranium.

Keywords: Uranyl-phosphoylide complex; Resonance stabilization; Diketo ylide

1. Introduction

Phosphorus ylides occupy a unique position in the chemistry of carbanions both as reagents and as ligands. Resonance stabilized ylides of the type Ph_3PCRR' (where $R = COCH_3$, COPh, COOEt, $CONH_2$, CN and $R' = H$, $COCH_3$, COPh) are significant for the variety in their coordination behaviour [1–3]. Resonance delocalization bestows ambidentate character to the ylides when they act as ligands; they form complexes with a variety of metal ions. Examples include ylide complexes of Pd(II) [4], Pt(II) [5], Rh(I) [6], Ti(IV), Zr(IV), Hf(IV) [7], Cu(II) [8], Hg(II) [9], W(0) [10], Ag(I) [11], Au(I), Au(II) and Au(III) [12]. In addition, phosphonium salt [13] and metalate [14] formations often interfere in their reactions with hydrated metal salts. The monoketo ylides and C,C-disubstituted ylides differ in their reactivity towards metal derivatives, for e.g., O-coordination of the monoketo ylide was observed with trimethyltin chloride [15], whereas the reaction of $Ph_3PC(COCH_3)(COPh)$ (ABPPY) with the same tin substrate did not yield the direct complexation product but led to decomposition to

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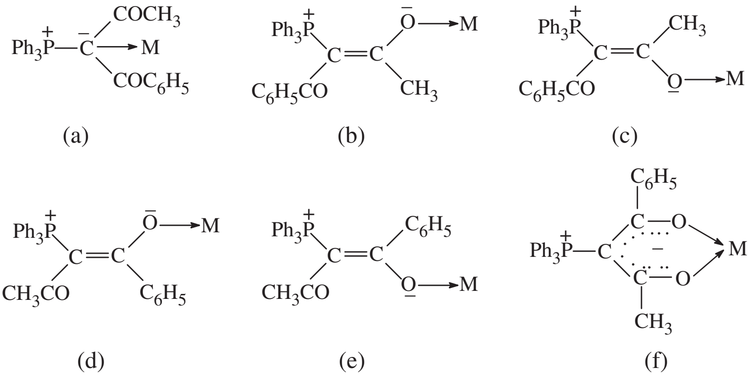

Scheme 1. The possible bonding modes of ABPPY to metal M.

$C_6H_5C{\equiv}CCO_2Me$ and $Me_3SnCl \cdot Ph_3PO$ [16]. Reactions of the monoketo ylide $Ph_3PCHCOPh$ with $UO_2(NO_3)_2 \cdot 6H_2O$ and $Ph_3PCHCOOCH_2CH_3$ with $UO_2(CH_3COO)_2 \cdot 2H_2O$ in 1 : 1 molar ratio yielded the corresponding phosphonium metalates [17].

Coordination of the diketoylide can occur via several bonding modes (scheme 1). In order to probe the bonding mode of the title ylide to U(VI), the reaction was carried out as part of our interest in ylides as extractants for precious metals from nuclear waste [18]. Recently, we synthesized the 2 : 1 complex of the title ylide and $UO_2(NO_3)_2$ in ice cold temperature, where the ylide is found to be coordinated via acetyl oxygen [17]. Herein, we report the reaction of the same reactants at room temperature yielding a 1 : 1 $ABPPY \cdot UO_2(NO_3)_2$ complex where the ylide is coordinated via both the acetyl and benzoyl oxygens in a chelating fashion. This represents the first example of the chelating mode of coordination of ABPPY to any metal.

2. Experimental

2.1. *Instrumentation*

Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer using KBr pellets. The ^1H, ^{31}P-$\{^1H\}$ and ^{13}C-$\{^1H\}$ NMR spectra were recorded on JEOL GSX 400 spectrometer operated on 399.55, 161.70 and 100.40 MHz, respectively. The chemical shifts were referenced relative to external tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra and 85% phosphoric acid for ^{31}P NMR spectra. Elemental analysis was performed at the Central Drug Research Institute, Lucknow, India.

2.2. *Synthesis*

2.2.1. α-acetyl-α-benzoylmethylenetriphenylphosphorane (ABPPY). The ligand ABPPY was prepared by the acetylation of benzoylmethylenetriphenylphosphorane (BPPY) as reported previously [19]. IR (cm^{-1}): 1587(m), 1565(m), 1535(vs), 1482(s), 1439(s), 1420(m), 1361(s), 1332(vs), 1304(vs), 1187(w), 1172(s), 1160(w), 1147(m), 1112(m), 1104(s), 1069(w), 1023(m), 999(m), 926(vs), 866(w), 787(m), 750(m), 728(vs), 696(vs), 669(vs), 635(w), 597(m), 563(s), 519(vs), 496(vs). ^{1}H NMR ($CDCl_3$): 1.80(s), 7.37-7.79(m); ^{31}P NMR ($CDCl_3$): 16.5 (s); ^{13}C NMR ($CDCl_3$): 29.55(d, $^3J_{P-C}$: 7.6), 86.32 (d, $^1J_{P-C}$: 100.6), 126.13 (d, $^1J_{P-C}$: 93.0), 128.20 (s), 128.60 (d, $^3J_{P-C}$: 12.3), 129.0 (s), 130.81 (s), 131.63 (d, $^4J_{P-C}$: 3.1), 133.16 (d, $^2J_{P-C}$: 10.6), 143.41 (d, $^3J_{P-C}$: 9.1), 192.8 (d, $^3J_{P-C}$: 3.0), 193.5, $^3J_{P-C}$: 9.1).

2.2.2. (α-acetyl-α-benzoylmethylenetriphenylphosphorane-κO,O′)-dinitratodioxouranium(VI) [(ABPPY) · $UO_2(NO_3)_2$]. The title complex was synthesized by dropwise addition of a solution of 0.30 g (0.59 mmol) of $UO_2(NO_3)_2 \cdot 6H_2O$ in methanol to a methanolic solution of ABPPY (0.25 g, 0.59 mmol). The solution was then stirred overnight at room temperature. On removal of the solvent *in vacuo*, a yellow solid was obtained which was recrystallized from chloroform–hexane mixture. Yield: 0.42 g (88%); m.p. 498–499 K. Anal. Calcd for $C_{28}H_{23}N_2O_{10}PU$(%): C, 41.19; H, 2.83. Found: C, 41.23; H, 2.78. IR (cm^{-1}): 2923(w), 2853(w), 1635(m), 1591(m), 1573(m), 1528(vs), 1484(s), 1441(m), 1410(m), 1384(vs), 1338(m), 1284(vs), 1177(w), 1104(s), 1025(w), 999(w), 936(s), 891(w), 866(w), 808(w), 790(w), 751(m), 716(m), 694(s), 638(w), 618(w), 591(w), 570(m), 538(w), 513(m), 428(w). ^{1}H NMR (400 MHz, dmso-d6): 1.68(s), 7.42-8.24(m); ^{31}P NMR (162 MHz, dmso-d6): 16.1(s), ^{13}C NMR (100 MHz, dmso-d6): 29.43(d, $^3J_{PC} = 7.6$), 85.76(d, $^1J_{PC} = 102.1$), 126.08(d, $^1J_{PC} = 91.4$), 128.66(s), 128.94(s), 129.10(d, $^3J_{PC} = 12.2$), 131.18(s), 132.18(s), 133.09(d, $^2J_{PC} = 10.6$), 143.48(d, $^3J_{PC} = 9.1$), 191.18(d, $^2J_{PC} = 3.0$), 192.72(d, $^2J_{PC} = 9.1$)

2.3. *Crystal structure determination*

X-ray intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo-Kα radiation at the Indian Institute of Technology-Madras, Chennai, India. The structure was solved by direct methods using the programme SHELXS-97 [20]. The refinement and all further calculations were carried out using SHELXL-97 [21]. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. Empirical absorption correction was applied to the data via PSI-SCANS. The strongest peak on the final difference Fourier map had a density of 3.28 e Å^{-3} around uranium at a distance of 1.005 Å. Crystal data and refinement details are given in table 1.

3. Results and discussion

The reaction of ABPPY with uranyl nitrate hexahydrate in methanol at room temperature yields the title complex in which the ligand is bidentate chelating, in contrast to the same reaction carried out at (273 K) with a 2 : 1 coordination of the ylide to metal through the acetyl oxygen [17].

The stoichiometry of the title complex has been established by elemental analysis. The ν_{CO} of the COMe and COPh groups in ABPPY observed at 1535 cm^{-1} and

Table 1. Crystals data and refinement details.

Empirical formula	$C_{28}H_{23}N_2O_{10}PU$
Formula Weight	816.48
Temperature (K)	293(2)
Wavelength	0.71073
Crystal system, Space group	Monoclinic, $P2_1/n$
Unit cell dimensions (Å, °)	
a	10.007(2)
b	15.285(7)
c	19.20(1)
β	91.22(3)
V (Å^3)	2936(2)
Z	4
D_c (g cm^{-3})	1.847
Absorption coefficient (mm^{-1})	5.643
F(000)	1568
θ range for data collection	2.1 to 24.8
Index ranges	$0 \le h \le 11$, $0 \le k \le 18$, $-22 \le l \le 22$
Reflections collected/unique	5463/5146 [$R_{int} = 0.0927$]
Data/restraints/parameters	5146/0/332
Goodness-of-fit on F^2	1.123
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0794$, $wR_2 = 0.1855$
R indices (all data)	$R_1 = 0.1204$, $wR_2 = 0.2319$
Largest diff. peak and hole (e A^{-3})	3.280 and −5.592

1565 cm^{-1} are shifted downward by 7 cm^{-1} and upward by 8 cm^{-1} respectively, in the title complex. There is little change in the local symmetry of ABPPY after complexation. Accordingly, very similar ^{1}H, ^{31}P and ^{13}C signals were observed in the NMR spectra for the title complex when compared to those observed for the parent ylide. This may indicate not only lack of C-coordination but also a preferential symmetrical coordination of ABPPY to uranium. The NMR data support the structure proposed by single crystal X-ray analysis.

The bidentate symmetrical chelation of ABPPY with uranyl nitrate in the title complex has been confirmed by single crystal X-ray diffraction analysis (figure 1, scheme 1f) and is in contrast to monodentate coordination of the same ylide through the COMe group to Hg(II) (scheme 1b) [22]. The oxygens of the keto groups are *trans* oriented with respect to P$^+$ center as shown by the corresponding torsion angles (table 2). The dodecahedral eight-coordinate geometry of U(VI) is quite different to the hexagonal bipyramidal geometry of uranyl nitrate hexahydrate [23]. The two quartets of atoms, O1 O8 O2 O4 and O6 O5 O3 O7 form planes each of which contains the uranium atom, making a dihedral angle of 88.1(4)°, indicating a triangulated dodecahedral coordination around uranium. The distances, P–C$_{ylide}$ [1.751(4) Å], C–C$_{acetyl}$ [1.430(5) Å], C–C$_{benzoyl}$ [1.453(5) Å], C–O$_{acetyl}$ [1.268(5) Å] and C–O$_{benzoyl}$ [1.232(5) Å] in the free ylide do not change much after chelation of uranyl nitrate and suggest a similar delocalization of the ylidic electron density. However, in the 2 : 1 complex, [(ABPPY)$_2$UO$_2$(NO$_3$)$_2$] [17], the elongation of the P–C$_{ylide}$ [1.771(4) Å], C–C$_{benzoyl}$ [1.490(5) Å] and C–O$_{acetyl}$ [1.283(4) Å] as well as the significant shortening of C–C$_{acetyl}$ [1.383(5) Å] is in accordance with unidirectional delocalization of electron density towards the acetyl group. The formation of the title complex requires not only the elimination of water from the coordination sphere but also a reorganization of the coordination environment. Despite this reorganization both the oxo and nitrate groups

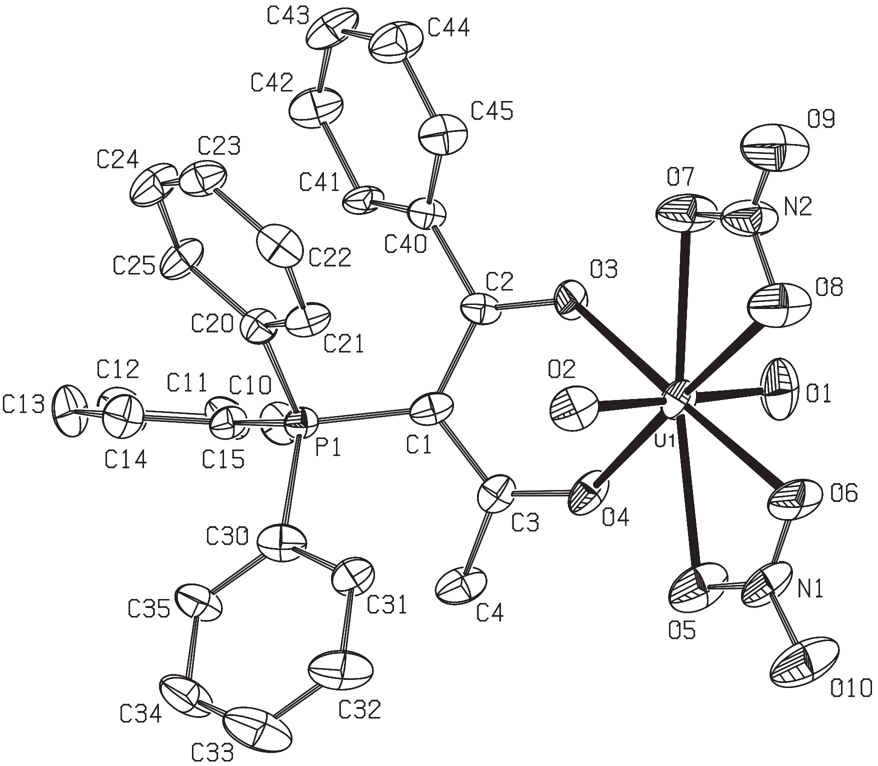

Figure 1. Molecular structure of [(ABPPY) · $UO_2(NO_3)_2$]. Hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å), bond angles (°) and torsion angles (°).

U1–O1	1.727(14)	U1–O5	2.512(14)
U1–O2	1.757(12)	U1–O6	2.509(11)
U1–O3	2.385(9)	U1–O7	2.518(12)
U1–O4	2.398(10)	U1–O8	2.487(13)
P1–C1	1.748(17)	C3–O4	1.254(17)
O5–N1	1.274(18)	O6–N1	1.244(19)
O10–N1	1.212(18)	O7–N2	1.29(2)
O8–N2	1.24(2)	O9–N2	1.17(2)
C2–O3	1.226(17)	C1–C2	1.48(2)
C1–C3	1.43(2)	C3–C4	1.49(2)
C2–C40	1.476(15)	P1–C10	1.804(7)
P1–C20	1.807(7)	P1–C3O	1.823(8)
C3–C1–C2	116.8(14)	C3–C1–P1	121.7(12)
C2–C1–P1	121.2(10)	O3–U1–O4	65.4(4)
O1–U1–O2	178.7(6)	O8–U1–O6	62.6(4)
O4–C3–C1	122.5(14)	O3–C2–C1	122.2(13)
C3–O4–U1	131.5(9)	C2–O3–U1	131.2(9)
P1–C1–C2–O3	154.5(12)	P1–C1–C3–O4	−152.1(12)

exhibit no intraligand structural change, when compared to the structure of uranyl nitrate hexahydrate.

Mulliken population analysis [24] based on *ab initio* calculation at the MP2/6–31 G* level on the model ylide, $H_3PC(COMe)(COPh)$ shows that the negative charge is delocalized among the ylidic carbon and the two oxygen centers, the charges on the ylidic carbon, the oxygen of the acetyl and the oxygen of the benzoyl groups are -0.603, -0.686 and -0.637 respectively. The PM3 calculation [24] of the proton affinity for $Ph_3PC(COMe)(COPh)$ for all three sites differ within 2 kcal mol^{-1}, indicating that all three are equally probable sites for protonation. Similar trend is expected for complexation. The present results reveal that coordination is through both oxygen atoms of the ylide, ABPPY, in a chelating fashion. We attribute the formation of the title complex to the oxophilic character of uranium as well as the hardness of the diketoylide.

Supplementary material

Crystallographic data for the structure analysis has been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 236875). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033, E-mail: deposit@ccdc.cam.ac.uk).

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