J. Chem. Research (S),
2001, 50–51
J. Chem. Research (M),
2001, 0236–0250

Synergistic complexes of tributyl phosphate and dibutyl (butyl) phosphonate with uranyl bis(β-diketonates). Synthesis, characterisation and molecular structure of [$UO_2(TTA)_2$.TIBP]

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Tributyl phosphate or dibutyl (butyl) phosphonate complexes of the type [UO_2 $(OO)_2$.X] (OO = TTA or DBM ; X = TBP, TIBP or DBBP) have been prepared and characterised by ^1H and $^{31}P\{^1H\}$ NMR, IR and elemental analyses. The structure of complex [$UO_2(TTA)_2$.TIBP] shows that the TIBP ligand coordinates through its phosphoryl oxygen atom to the uranyl ion.

Keywords: synergistic complexes, uranyl bis(β-diketonates)

In continuation of our studies on synergistic complexes of uranyl bis (β-diketonates) with neutral ligand,[3, 5] we report here the tributyl phosphate and dibutyl (butyl) phosphonate complexes of uranyl bis β-diketonates of the type [$UO_2(OO)_2$.X] (OO = TTA or DBM; X = TBP, TIBP or DBBP] and their characterization by various spectroscopic and single crystal X-ray diffraction methods.

Reaction of [UO_2 $(OO)_2$.$2H_2O$] with one equivalent of tributyl phosphate or dibutyl (butyl) phophonate in benzene yielded an adducts of the type [UO_2 $(OO)_2$.X] (where OO = TTA or DBM; X = TBP ,TIBP or DBBP). IR spectra of all complexes show that the ν_{OH} (3200–3500 cm^{-1}) for H_2O molecules of the starting complex [UO_2 $(OO)_2$.$2H_2O$] has completely disappeared. It indicates that the water molecules are replaced by tributyl phosphate or phosphonate ligand. Spectra further show that the ν_{PO} (1190–1225 cm^{-1}) in the complexes has been shifted to lower frequencies compared to the free ligand (ν_{PO} = 1275 cm^{-1}), indicating the coordination of the phosphoryl oxygen atoms of phosphate/ phosphonate ligands to the uranyl group. The observed frequency difference $\Delta\nu_{PO}$ ($\Delta\nu = \nu_{\text{free ligand}} - \nu_{\text{complex}}$) agrees well with the structurally characterized complexes in which the ligand coordinates through its phosphoryl oxygen atom. This is further supported by $^{31}P\{^1H\}$ NMR spectra, (Table 1) which show a single resonance for all complexes which appears at ca 3–8 ppm downfield relative to the free ligands (δ = –0.12 , –0.39 and 31.93 ppm respectively for TBP, TIBP or DBBP).

Table 1 Analytical, m.p, IR, ^1H and $^{31}P\{^1H\}$ NMR data for complexes [$UO_2(OO)_2$.X]

Complexes	M.p. (C°)	Analysis (%) Found (Calcd)		ν	δ_P	δ_H
		C	H			
[$UO_2(TTA)_2$.TBP]	110	34.4 (34.4)	3.6 (3.6)	1590(CO,TTA); 1190(PO, TBP); 915(O=U=O)	3.22	0.91 (t, CH_3, ^3J(HH) 7.5 Hz, TBP); 1.43 (m, ^3J(HH) 7.5 Hz, CH_2, TBP); 1.75 (m, ^3J(HH) 6.5 Hz, CH_2, TBP); 4.52 (m, ^3J(PH) 13 Hz, ^3J(HH) 6 Hz, OCH_2, TBP); 6.79, 6.82 (s, CH, TTA); 7.25–7.3 (m, C_4H_3S, TTA); 7.8– 7.84 (m, C_4H_3S, TTA), 8.1–8.3 (m, C_4H_3S, TTA).
[$UO_2(TTA)_2$.TIBP]	142	34.4 (34.4)	3.6 (3.6)	1590(CO,TTA); 1200(PO,TIBP); 915(O=U=O).	2.83	0.96 (d, CH_3, ^3J(HH) 6 Hz, TIBP); 2.05 (m, CH , TIBP); 4.27 (m, ^3J(PH) 6 Hz, ^3J(HH) 6 Hz, OCH_2, TIBP); 6.78, 6.81 (s, CH, TTA); 7.25–7.32 (m, C_4H_3S, TTA); 7.8–7.85 (m, C_4H_3S, TTA), 8.2–8.3 (m, C_4H_3S, TTA).
[$UO_2(DBM)_2$.TBP]	105	51.0 (51.3)	4.9 (5.0)	1590(CO, DBM); 1215(PO, TBP); 915(O=U=O).	3.17	0.83 (t, 9H, CH_3, ^3J(HH) 7 Hz, TBP); 1.29 (m, ^3J(HH) 7 Hz, 6H, CH_2, TBP); 1.61 (m, 6H, CH_2, TBP); 4.38 (m, ^3J(PH) 13 Hz, ^3J(HH) 7 Hz, 6H, OCH_2, TBP); 7.22 (s, 2H, CH, DBM); 7.53–7.6 (m, 12H, C_6H_5, DBM); 8.5 (br, 8H, C_6H_5, DBM)
[$UO_2(DBM)_2$.TIBP]	160	51.3 (51.3)	5.0 (5.0)	1590(CO, DBM); 1225(PO,TIBP); 910 (O=U=O).	2.84	0.85 (d, 18H, CH_3, ^3J(HH) 7 Hz, TIBP); 1.93 (m, 3H, CH, TIBP); 4.15 (m, 6H, OCH_2, TIBP); 7.22 (s, 2H, CH, DBM); 7.54–7.58 (m, 12H, C_6H_5, DBM); 8.5 (br, 8H, C_6H_5, DBM).
[$UO_2(TTA)_2$.DBBP]	90	34.7 (34.9)	3.6 (3.6)	1590(CO,TTA); 1190(PO, DBBP); 915(O=U=O)	39.4	0.91 (t, 9H, CH_3, ^3J(HH) 7.5 Hz, DBBP); 1.43–1.83 (m, 12H, CH_2, DBBP); 2.33 (m, 2H, PCH_2, DBBP); 4.55 (m, 4H, OCH_2, DBBP); 6.79, 6.82 (s, CH, TTA); 7.31 (m, 2H, C_4H_3S, TTA); 7.83 (m, 2H, C_4H_3S, TTA), 8.27 (m, 2H, C_4H_3S, TTA).
[$UO_2(DBM)_2$.DBBP]	95	52.0 (52.2)	5.2 (5.1)	1590(CO,TTA); 1215(PO, DBBP); 915(O=U=O)	38.5	0.77 (t, 3H, CH_3, ^3J(HH) 7 Hz, DBBP); 0.85 (t, 6H, CH_3, ^3J(HH) 7 Hz, DBBP); 1.22–1.62 (m, 10H, CH_2, DBBP); 1.69 (m, 2H, P-C-CH_2, DBBP); 2.22 (m, 2H, PCH_2, DBBP); 4.43 (m, 4H, OCH_2, DBBP); 7.20 (s, 2H, CH, DBM); 7.57 (m, 12H, C_6H_5, DBM); 8.44 (br, 8H, C_6H_5, DBM).

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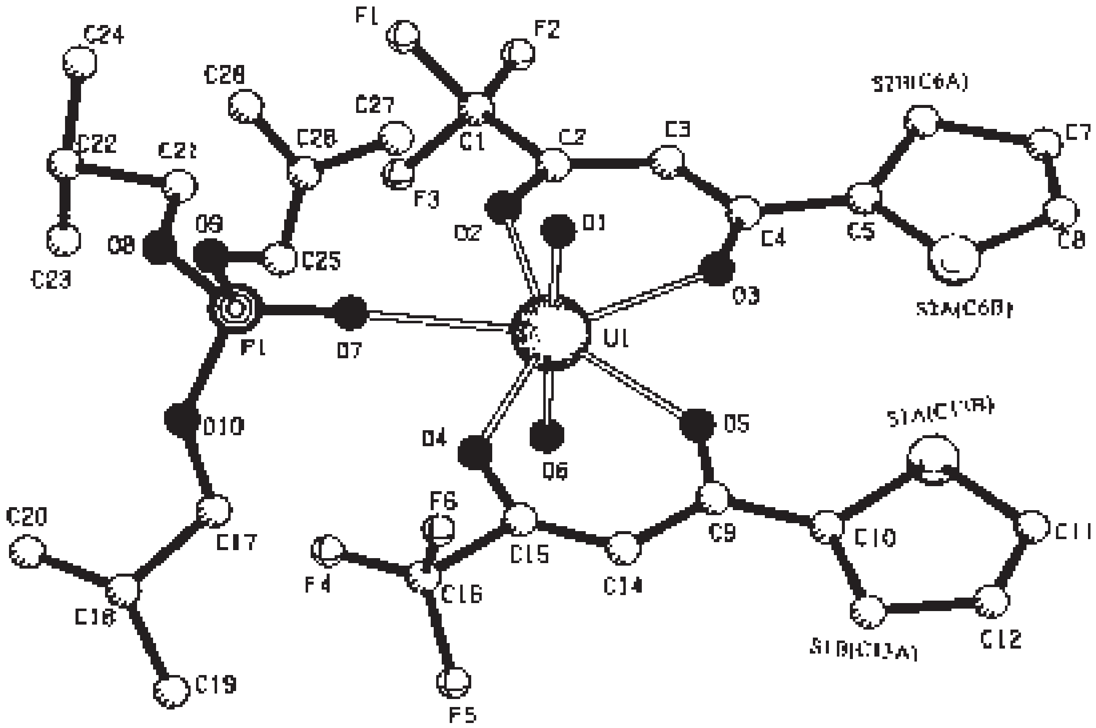

Fig. 1 Molecular structure of complex [$UO_2(TTA)_2$.TIBP] [Selected inter atomic distances (Å) and angles (°) : U(1)-O(1) 1.733(7), U(1)–O(6) 1.740(6), U(1)–O(5) 2.340(6), U(1)–O(4)2.400(6), U(1)–O(3) 2.370(6), U(1)–O(2) 2.374(6), U(1)–O(7) 2.403(7), O(1)–U(1)–O(6) 178.7(3), O(2)–U(1)–O(7) 72.3].

The ^1H NMR spectra of all complexes show the expected peak multiplicities and integrations. The OCH_2 protons of the phosphate/phosphonate ligands show the downfield shift of ca 0.40–0.60 ppm in all complexes relative to free ligands (δ_{OCH2} = 3.96, 3.67 and 3.95 ppm respectively for the TBP, TIBP or DBBP). This observation further supports the coordination of phosphate/phosphonate ligands to the uranyl group. The methylene proton of the β-diketonate ring gave two resonances for the TTA ligand, indicating that the TTA complexes exist as a mixture of two isomeric product,[3, 5] *cis* and *trans*. The structure of one, the complex [$UO_2(TTA)_2$.TIBP] has been determined by single crystal X-ray diffraction methods (for other compounds, we could not get proper crystals suitable for X-ray diffraction) and which confirms the spectroscopic observations.

The structure of the molecule [$UO_2(TTA)_2$.TIBP] is shown in Fig 1. It comprises of one uranium atom surrounded by seven oxygen atoms in a pentagonal bipyramidal geometry. The four oxygen atoms of TTA and one oxygen atom of TIBP form a planar pentagon, the two oxygens of the uranyl group lying above and below the plane. The bond lengths $U–O_{(uranyl\ oxygen)}$ [1.733(7), 1.740(6) Å][3], and $U-O_{(TTA)}$ [2.340(6), 2.370(6), 2.374(6), 2.400(6) Å][3,5] are within the expected values. The $U–O_{(phosphate)}$ distance [2.403(7) Å] is comparable with other related complexes.[3a,b] The other bond lengths and angles are normal.

The synergism in solvent extraction separation of uranyl ion by using a mixture of β-diketones and tributyl phosphate or dibutyl (butyl) phosphonate is due to adduct complex formation, in which the phosphate/phosphonate ligands coordinats through phosphoryl oxygen atoms to the uranyl ion. The X-ray structural studies of the complex [$UO_2(TTA)_2$.TIBP] confirms the spectroscopic observations.

Crystal data [$C_{28}H_{35}F_6O_{10}PS_2U$, Mr = 978.7, monoclinic, space group P21/c, *a* = 20.694(6), *b* = 19.3258(6), *c* = 9.6119(3) Å, β = 97.984 (1)°, Z = 4, Dc = 1.713 mg /m^3, F(000) = 1904, Data were collected at room temperature on Siemens SMART CCD diffractometer. The structure was solved by direct methods and the final *R* value is 0.0635.

The author (SK) is thankful to Shri. Rajendra Prasad and Dr. V. Venugopal, Head, Fuel Chemistry Division for their support. HKF would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 305/pfizik/622004. SSSR thanks the Universiti Sains Malaysia for a Visiting Post-Doctoral Fellowship.

Technique used: IR, ^1H, ^{31}P NMR, X-ray diffraction.

Reference: 12

Table 1: Analytical, m.p, IR, ^1H, and $^{31}P\{^1H\}$ NMR data for [$UO_2(OO)_2$.X].

Table 2. Summary of crystal data , collection parameters and refinement details for [$UO_2(TTA)_2$.TIBP].

Table 3. Atomic coordinates and equivalent isotropic displacement parameter for [$UO_2(TTA)_2$.TIBP].

Table 4. Selected inter atomic distances (Å) and angles (°) for [$UO_2(TTA)_2$.TIBP].

Received 1 September 2000; accepted 28 November 2000
Paper 00/497

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