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Preparation and Crystal and Molecular Structures of Uranyl Complexes of 4-Benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione and the Pyrazol-3-one Analogue

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Abstract

Uranyl complexes of the ligands 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione (Hbmppt), the 3-one analogue (Hbmpp), and the corresponding anions were prepared and characterized by elemental analysis and spectroscopic methods. The complexes $UO_2(NO_3)_2(Hbmppt)\cdot$acetone and $UO_2(NO_3)_2(Hbmpp)\cdot$acetone can be isolated from the reaction of $UO_2(NO_3)_2\cdot6H_2O$ and Hbmppt or Hbmpp in acetone. In ethanol, $UO_2(NO_3)_2\cdot6H_2O$ reacts with K(bmppt) or Hbmpp to give $UO_2(bmppt)_2\cdot2EtOH$ or $UO_2(bmpp)_2\cdot2EtOH$, respectively. The ethanol adducts will react with dimethylsulfoxide to yield the dmso complexes $UO_2(bmppt)_2(dmso)\cdot$acetone and $UO_2(bmpp)_2(dmso)$. $UO_2(NO_3)_2(Hbmppt)\cdot$acetone crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.663(5)$, $b = 11.522(4)$, $c = 11.823(3)$ Å, $\alpha = 78.18(3)$, $\beta = 72.56(3)$, $\gamma = 76.54(4)°$, $Z = 2$, $V = 1208.3$ Å^3, $\rho_{calc} = 2.05$ g cm^{-3}, $R_F = 0.031$, $R_{wF} = 0.038$. The crystal structure shows two bidentate nitrate anions and a neutral bidentate Hbmppt ligand (U–S = 2.871(3) Å) in the equatorial plane of the UO_2^{2+} ion. The Hbmppt ligand is bound as the N–H tautomer with a hydrogen bond between the N–H group and the oxygen atom of the acetone of crystallization (N···O = 2.71 Å). $UO_2(bmppt)_2(dmso)\cdot$acetone crystallizes in the monoclinic space group $P2_1/n$ with $a = 16.010(2)$, $b = 11.050(2)$, $c = 23.084(4)$, $\beta = 98.77(2)°$, $Z = 4$, $V = 4035.7$, $\rho_{calc} = 1.63$ g cm^{-3}, $R_F = 0.052$, $R_{wF} = 0.090$. The crystal structure shows discrete molecules of $UO_2(bmppt)_2(dmso)$ with a pentagonal bipyramidal geometry. The UO_2^{2+} group is coordinated with two bidentate bmppt anions and the oxygen of a dmso molecule in the equatorial plane. The bmppt anions are bound quite unsymmetrically. The dihedral angle between the plane of one bmppt anion (U–S = 2.836(6), U–O = 2.36(1) Å) and the uranyl equatorial plane is 38.5° while for the other bmppt anion (U–S = 2.902(6), U–O = 2.29(1) Å) the dihedral angle is only 11°.

Introduction

The actinide coordination chemistry of ligands containing sulfur donor atoms is largely unexplored. One historical reason for this limited interest is that under the aerobic, highly acidic conditions commonly used for processing the actinides, sulfur donor ligands can be readily oxidized or hydrolyzed and often bind weakly to the 'hard' metal ions relative to the oxygen donor ligands present. In recent years, however, it has become increasingly recognized that these softer donor sites, especially when combined with oxygen donors in multidentate ligands or synergistic systems, have considerable promise for increasing and controlling the selectivity of complexation relative to the extensively explored oxygen donor systems. The work of Musikas and coworkers has been especially important in demonstrating the potential of several sulfur and nitrogen donor ligands for effecting separations of the trivalent actinides and lanthanides in various liquid–liquid extraction systems [1, 2].

Clearly a more detailed investigation of the coordination chemistry and extraction behavior of some sulfur donor ligands is necessary to obtain a more general understanding of their capabilities for analysis and separation of the actinides. One class of ligands of interest is the monothio derivatives of the 1,3-dicarbonyls. These compounds have been investigated as analytical reagents for the transition metals [3], but relatively little work has been done with the actinides and lanthanides. The compound thiothenoyltrifluoroacetone has been most studied, including some work with U(VI) [3]. However, the monothio analogues of 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (Hbmpp) offer some advantages in that they appear more stable to oxidation in solution and can extract transition

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metal ions from more acidic solution than can thiothenoyltrifluoroacetone [4, 5]. This paper reports the synthesis and characterization of uranyl complexes of 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione (Hbmppt) and the parent compound Hbmpp.

Experimental

General Information

Reagent grade solvents and uranyl nitrate hexahydrate were used as received from Aldrich Chemical Co. and Alfa Products, respectively. Elemental analyses were done by Galbraith Laboratories, Inc. Infrared and NMR spectra* were recorded on Perkin-Elmer Model 683 and Varian Model EM390 spectrometers, respectively.

Preparation of Compounds

4-Benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione (Hbmppt)

Compound Hbmppt was synthesized from 1-phenyl-3-methyl-4-benzoyl-5-chloropyrazole by a procedure similar to that of Michaelis [6] by refluxing (5 h) 0.1 mol of the chloropyrazole with $NaSH \cdot H_2O$ (4 equivalents) in ethanol (320 ml). The nitrogen-purged reaction mixture was cooled and allowed to settle. The product was isolated by transfer (reduced pressure) of the supernatant liquid through a teflon tube (care must be taken not to agitate the solids) and by subsequent *in vacuo* reduction of the solvent volume by *ca.* one-half. Water (400 ml) was added and the solution (pH 9–10) was extracted with $CHCl_3$ (50 ml) to remove neutral materials. The aqueous layer was made acidic (pH 5–6) with 100 ml of 3 M HCl and extracted 3 times with $CHCl_3$ (100 ml each). The organic fractions were combined, washed with 100 ml of H_2O, and dried over anhydrous Na_2SO_4. The solvent was subsequently removed under vacuum and the solid residue dissolved in hot ethanol (50 ml) and recrystallized to yield 25 g (78%) of air stable orange crystals, m.p. 111–112 °C. ^1H NMR ($CDCl_3$/TMS): 2.05 δ (s, CH_3, 3H), 7.2–7.9 δ (m, Ph + acidic proton, 11H); (dmso-d_6/TMS): 2.25 δ (s, CH_3, 3H), 3.65 δ (s, SH, 1H), 7.1–7.8 δ (m, Ph, 10H); (ethanol-d_6/TMS): 1.93 δ (s, CH_3, 3H), 5.01 δ (s, acidic proton chemically exchanging with ethanol OH), 7.2–7.6 δ (m, Ph, 10H); IR (KBr): 3050w, 2992w, 2987w, 2925w, 2400w, br (ν_{S-H}), 1600s, 1576m, 1504vs, 1462(sh), 1449m, 1435vs, 1420(sh), 1386s, 1367m, 1335w, 1323w, 1297w, 1285ms, 1253(sh), 1243mw, 1181mw, 1163m, 1094w, 1070mw, 1036mw, 1030mw, 1008s, 972w, 947ms, 929ms, 912(sh), 900ms, 837w, 801mw, 767vs, 750s, 704vs, 695vs, 689s, 664m, 650m, 622w, 612w, 553m, 517w, 489mw, 410w, 389mw, 344mw, 308mw cm^{-1}. UV: benzene λ_{max} 284 ($\epsilon = 1.5 \times 10^4$), 420 ($\epsilon = 4.0 \times 10^2$) nm. *Anal.* Calc. for $C_{17}H_{14}N_2OS$: C, 69.36; H, 4.79; N, 9.52; O, 5.44; S, 10.89. Found: C, 69.11; H, 4.72; N, 9.20; O (by diff.), 5.90; S, 11.07%.

If the reaction mixture was not handled carefully during the above procedure, a substantial amount of an oxidation product was produced. This material was isolated from the mother liquor as yellow crystals and identified as the disulfide dimer of Hbmppt, m.p. 156–157 °C. ^1H NMR ($CDCl_3$/TMS): 2.28 δ (s, CH_3, 3H), 7.2–7.9 δ (m, Ph, 10H); (dmso-d_6/TMS): 2.28 δ (s, CH_3, 3H), 7.1–7.8 δ (m, Ph, 10H). IR (KBr): 3060mw, 2965w, 2926w, 1642vs, 1594s, 1577m, 1504vs, 1459vs, 1434s, 1383s, 1310w, 1298w, 1280s, 1226m, 1176mw, 1154m, 1106w, 1075m, 1027w, 1009ms, 930m, 903vs, 848w, 836mw, 810w, 780(sh), 766s, 739s, 696vs, 673m, 666m, 654ms, 619mw, 611w, 601m, 500m, 329mw cm^{-1}. No SH peak observed. UV: $CHCl_3$ λ_{max} 258 ($\epsilon = 1.8 \times 10^4$), 288(sh) nm. *Anal.* Calc. for $C_{34}H_{26}N_4O_2S_2$: C, 69.60; H, 4.47; N, 9.55; O, 5.45; S, 10.93. Found: C, 69.32; H, 4.52; N, 9.38; O (by diff.), 5.62; S, 11.16%.

$UO_2(NO_3)_2$(Hbmppt)·acetone

Under argon, adding $UO_2(NO_3)_2 \cdot 6H_2O$ (4 mmol) to a solution of Hbmppt (4 mmol) in 40 ml of acetone caused a rapid color change from orange to deep red. The solution was filtered through a medium glass frit. Heptane was added dropwise to the stirring filtrate while it was heated in a 60–65 °C water bath. When cloudiness persisted after the heptane was added (≈40 ml), the stirring was stopped and the solution allowed to cool slowly to room temperature. A crop of dark orange crystals was collected by filtration, washed with 3 × 10 ml of 1:1 acetone/heptane, and dried under vacuum. Yield 1.22 g (41%). ^1H NMR: In dmso-d_6 the red–orange complex dissolved to give a yellow solution with proton resonances identical to those of the free ligand in dmso-d_6 (see Hbmppt data above) plus a singlet at 2.03 δ from acetone. In ethanol-d_6 the complex is slightly soluble and yielded an orange solution with phenyl and methyl resonances similar to that of $UO_2(bmppt)_2 \cdot 2EtOH$ in ethanol-d_6 plus a singlet from acetone at 2.09 δ and a sharp singlet caused by acidic protons (HNO_3, Hbmppt, etc.) chemically exchanging rapidly with ethanol at 5.06 δ. Some differences in the complex phenyl multiplet relative to $UO_2(bmppt)_2 \cdot 2EtOH$ could be attributed to the presence of free Hbmppt. IR (Nujol mull, reacts with KBr): 1691ms, 1598(sh), 1593ms, 1574m,

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*The following abbreviations were used in reporting the spectra: NMR, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; IR, vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

1558m, 1513vs, 1494vs, 1387m, 1289ms, 1272ms, 1244w, 1166m, 1036mw, 1028m, 948w, 935vs, 924w, 857mw, 805m, 769m, 743s, 709m, 694m, 671w, 660w, 621w, 604mw, 567m, 554w, 423w cm^{-1}. *Anal.* Calc. for $C_{20}H_{20}O_{11}N_4U$: C, 32.18; H, 2.70; N, 7.51; S, 4.30. Found: C, 32.22; H, 2.82; N, 7.57; S, 4.30%.

$UO_2(NO_3)_2$(Hbmpp)·acetone

Adding 5.02 g (10.0 mmol) of $UO_2(NO_3)_2\cdot 6H_2O$ to a stirring solution of Hbmpp (2.79 g, 10.0 mmol) in 70 ml of acetone caused a rapid color change from yellow to orange. Addition of 70 ml of heptane as described above for the Hbmppt complex yielded a crop of yellow crystals that was collected by filtration, washed with 3 X 20 ml of 1:1 acetone/heptane, and dried under vacuum. Yield 4.07 g (56%). ^1H NMR: In dmso-d_6 the yellow complex dissolved to give an orange solution with a sharp singlet from acetone at 2.04 δ, three singlets of pyrazolone-CH_3 groups attributed to UO_2(bmpp)$_2$-(dmso) (1.89 δ), free Hbmpp (2.19 δ), and an unknown species (2.38 δ), a complex phenyl multiplet (6.9–8.3 δ), and a broad resonance at 10.08 δ from the acidic protons. Initially the relative areas of the pyrazolone-CH_3 groups were 50:10:40 (1.89:2.19: 2.38 δ), but after 48 h at room temperature (RT) this changed to 37:16:47 and the broad resonance shifted into the phenyl region, 6.8–8.5 δ. Yellow crystals of $UO_2(NO_3)_2$(Hbmpp)·acetone (0.193 g) dissolved in 2 ml of warm ethanol gave an orange solution. Orange crystals of UO_2(bmpp)$_2$·2EtOH began to deposit after 5–10 min. The yield of UO_2-(bmpp)$_2$·2EtOH isolated after 1 h was 0.073 g (61% assuming reaction proceeds to give equal amounts of UO_2(bmpp)$_2$·2EtOH and soluble uranyl nitrate). By using ethanol-d_6, the ^1H NMR spectrum of the material remaining in solution was obtained and showed phenyl and pyrazolone CH_3 resonances similar to UO_2(bmpp)$_2$(dmso) in ethanol-d_6 plus a large singlet due to excess acetone. IR (Nujol mull, reacts with KBr): 3170m, 3070m, 1692m, 1637vs, 1596m, 1534vs, 1485vs, 1450s, 1431s, 1386ms, 1307(sh), 1286s, 1251s, 1214m, 1174mw, 1164w, 1144mw, 1073mw, 1033ms, 1021ms, 1002w, 942vs, 920w, 870w, 851ms, 808mw, 776ms, 765ms, 757m, 746ms, 735ms, 709ms, 700ms, 676m, 658w, 612mw, 556mw, 510mw, 418mw cm^{-1}. *Anal.* Calc. for $C_{20}H_{20}O_{11}N_4U$: C, 32.89; H, 2.76; N, 7.67. Found: C, 33.08, 33.21; H, 2.88, 2.92; N, 7.73, 7.70%.

UO_2(bmppt)$_2$·2EtOH

Using Schlenk techniques, 0.587 g (2.00 mmol) of Hbmppt was stirred under argon with 10 ml of absolute EtOH. To the yellow solution and largely undissolved solid was added 0.124 g of KOH (2.2 mmol). The KOH and Hbmppt dissolved over 5–10 min to give an orange solution. $UO_2(NO_3)_2\cdot 6H_2O$ (0.502 g, 1.00 mmol) was added and a burgundy-red solution containing precipitated solid resulted. After the reaction mixture was stirred for 30 min, it was filtered under N_2 (fine frit) and washed with 5 X 1 ml of EtOH, yielding 0.181 g of off-white solid. The nearly opaque burgundy filtrate was stirred overnight under a slow argon flow. After 16 h, 2–3 ml of EtOH had evaporated and a powdery solid had formed. The red–brown solid was collected on a medium glass frit, washed with 3 X 1 ml of EtOH, and dried under vacuum. Yield 0.773 g (82%). ^1H NMR ($CDCl_3$/TMS): 1.17 δ, J_{HH} = 6.5 Hz (t, CH_3-EtOH, 6H), 1.80, 1.77 δ (two s, pyrazolone-CH_3, 3H each), 3.85 δ, J_{HH} = 6.3 Hz (q, CH_2-EtOH, 4H), 4.79 δ (s, broad, concentration-dependent chemical shift, 2H), 7.27, 7.65 δ (two m, Ph, 12H, 8H). IR (KBr): 3650–2600w, br, 3602w, 3058w, 2975w, 2930w, 1597m, 1581mw, 1525s, 1492s, 1472vs, 1454vs, 1428vs, 1392s, 1369(sh), 1292w, 1275w, 1225mw, 1153ms, 1081(sh), 1068mw, 1029m, 1000ms, 945m, 922s, 878w, 804m, 762ms, 747ms, 704ms, 692ms, 675w, 665w, 650mw, 625mw, 612w, 564m, 409mw cm^{-1}. UV: ethanol, λ_{max} 236 (ϵ = 3.7 X 10^4), 274 (ϵ = 2.1 X 10^4), 347 (ϵ = 4.4 X 10^3) nm. *Anal.* Calc. for $C_{38}H_{38}N_4O_6S_2U$: C, 48.10; H, 4.04; N, 5.90; S, 6.76. Found: C, 47.78, 47.71; H, 4.10, 4.12; N, 5.84, 5.74; S, 7.06, 7.00%.

UO_2(bmpp)$_2$·2EtOH

To a yellow solution containing 5.566 g (20.0 mmol) of Hbmpp in 150 ml of warm (50–60 °C) EtOH was added 5.030 g (10.0 mmol) of UO_2-$(NO_3)_2\cdot 6H_2O$. The orange solution that resulted was filtered while it was still warm and allowed to cool slowly to room temperature. After 24 h a crop of orange crystals was collected by filtration, washed with 3 X 50 ml of EtOH, and dried under vacuum. Yield 8.29 g (90%). ^1H NMR ($CDCl_3$/TMS): 1.19 δ (t, $^3J_{HH}$ 7 Hz, CH_3-EtOH, 6H), 1.93 δ (s, CH_3, 6H), 3.40 δ (q, $^3J_{HH}$ 7 Hz, CH_2-EtOH, 4H), 4.88 δ (s, broad, concentration-dependent chemical shift, OH-EtOH, 2H), 7.06, 7.36, 7.65, 8.04 δ (four m, Ph, 6H, 6H, 4H, 4H). IR (KBr): 3600–2400 m, br (OH), 3060w, 2975w, 2930w, 1615(sh), 1603s, 1593(sh), 1583s, 1568vs, 1526m, 1499m, 1474vs, 1460(sh), 1430m, 1379m, 1241w, 1161m, 1073m, 1058m, 1038m, 1025m, 951m, 923s, 910(sh), 877m, 841m, 837(sh), 768m, 760m, 732m, 705m, 699m, 690(sh), 658m, 620m, 611m, 558mw, 514mw, 412mw, 385w cm^{-1}. *Anal.* Calc. for $C_{38}H_{38}N_4O_8U$: C, 49.79; H, 4.18; N, 6.11. Found: C, 49.71; H, 4.32; N, 6.09%.

UO_2(bmppt)$_2$(dmso)·acetone

Under argon, 0.171 g (0.18 mmol) of UO_2-(bmppt)$_2$·2EtOH was dissolved in 1.5 ml of acetone, and 28 μl of dmso was added. Clumps of dark red crystals grew slowly over 24 h. The solution was decanted and the crystals washed with 2 X 0.5 ml of cold acetone. Vacuum drying for 5–10 min yielded 0.114 g (64%). ^{1}H NMR (acetone-d$_6$/TMS): 1.86 δ (s, pyrazolone-CH$_3$, 6H), 2.02 δ (s, CH$_3$-acetone, 6H), 2.93 δ (s, CH$_3$-dmso, 6H), 7.44, 7.87 δ (two m, Ph, 12H, 8H). IR (KBr): 3065w, 3015w, 2975(sh), 2912w, 1711ms, 1597ms, 1580m, 1524vs, 1493vs, 1476vs, 1454vs, 1428vs, 1391vs, 1367s, 1315mw, 1294mw, 1273mw, 1220ms, 1153s, 1079m, 1064m, 1024m, 998vs, 988(sh), 960(sh), 938s, 911vs, 859w, 842w, 800m, 765s, 746s, 704s, 694s, 686s, 674m, 665(sh), 651m, 631m, 556ms, 530mw, 512w, 492w cm^{-1}. UV: ethanol, λ_{max} 238 (ϵ = 4.6 X 10^4), 278 (ϵ = 3.0 X 10^4), 348 (center of broad shoulder, ϵ = 6.5 X 10^3) nm. *Anal.* Calc. for $C_{39}H_{38}N_4O_6S_3U$: C, 47.17; H, 3.86; N, 5.64; S, 9.69. Found: C, 47.04, 47.42; H, 3.81, 3.93; N, 5.65, 5.60; S, 9.86, 9.74%.

UO$_2$(bmpp)$_2$(dmso)

To a yellow solution of Hbmpp (1.12 g, 4.0 mmol) in 20 ml of dmso was added $UO_2(NO_3)_2 \cdot 6H_2O$ (1.003 g, 2.00 mmol). The resulting deep orange solution was filtered and warmed to 60–70 °C in a water bath while 4 ml of distilled water was added slowly dropwise with vigorous stirring. After the addition, the solution was allowed to cool slowly to room temperature. A crop of orange crystals was collected by filtration, washed with 2 X 5 ml of 4:1 dmso/H$_2$O, then with 3 X 15 ml of diethyl ether, and dried under vacuum. Yield 1.183 g (65%). Crystals of UO$_2$(bmpp)$_2$(dmso) can also be obtained by dissolving UO$_2$(bmpp)$_2$·2EtOH in warm dmso/H$_2$O and cooling the solution slowly to room temperature. Crystals of UO$_2$(bmpp)$_2$(dmso) suitable for an X-ray structure determination [7] were obtained by this procedure. m.p. 228–231 °C; ^{1}H NMR (CDCl$_3$/TMS): 1.89, 1.99 δ (overlapping singlets, CH$_3$, 6H), 2.69 δ (s, CH$_3$-dmso, 6H), 7.01, 7.33, 7.69, 8.09 δ (four m, Ph, 6H, 6H, 4H, 4H), (dmso-d$_6$/TMS): 1.94 δ (s, CH$_3$, 6H), 2.56 δ (s, CH$_3$-dmso, 6H), 7.13, 7.51, 7.78, 8.18 δ (four m, Ph, 6H, 6H, 4H, 4H); IR (KBr): 3059w, 2927w, 1602s, 1592s, 1581m, 1569vs, 1532m, 1498m, 1471vs, 1460s, 1436m, 1415m, 1405m, 1375ms, 1359m, 1158m, 1072m, 1055m, 1026m, 1014w, 1001m, 992(sh), 962(sh), 950m, 913s, 836m, 828w, 764ms, 751(sh), 731m, 710m, 704m, 693m, 656m, 621m, 611m, 553mw, 518w, 416m cm^{-1}. *Anal.* Calc. for $C_{36}H_{32}N_4O_7SU$: C, 47.90; H, 3.57; N, 6.21. Found: C, 47.83, 47.46; H, 3.56, 3.71; N, 6.23, 6.16%.

TABLE I. X-ray Data

	UO$_2$(bmppt)$_2$(dmso)·acetone	UO$_2$(NO$_3$)$_2$(Hbmppt)·acetone
Formula	$C_{36}H_{32}O_5S_3N_4U$	$C_{20}H_{20}O_{10}SN_4U$
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	16.010(2)	9.663(5)
b (Å)	11.050(2)	11.522(4)
c (Å)	23.082(4)	11.823(3)
α (°)		78.18(3)
β (°)	98.77(2)	72.56(3)
γ (°)		76.54(4)
V (Å^3)	4035.7	1208.3
Z	4	2
D_x (g cm^{-3})	1.63	2.05
I (Mo Kα_1)	0.70930	0.70930
Temperature (°C)	ambient	ambient
Crystal color	dark red	red–orange
Absorption coefficient (cm^{-1})	40.1	65.1
Absorption correction type	f + sphere	f + sphere
Sphere radius (mm)	0.2	0.2
Transmission (min, max)	0.36, 0.28	0.27, 0.14
Scan range (2θ max)	45°	45°
Scan type	θ–2θ	θ–2θ
Scan rate	variable	variable
($-h$, $+h$), ($-k$, $+k$), ($-l$, $+l$)	(17, 16) (0, 11) (0, 24)	(9, 9), (0, 12), (12, 12)
Total no. collected	5252	3160
With $I \geqslant 2\sigma(I)$	3246	2540
R_F equivalent reflections (%)	1.6	1.2
R_F observed reflections (%)	5.2	3.1
R_{wF} observed reflections (%)	9.0	3.8

Crystal Structure Solutions and Refinement

Data were collected on an Enraf Nonius CAD-4 diffractometer. Data collection methods and cell data are given in Table I. An absorption correction was made by measuring the intensity of a low angle reflection as a function of Ψ (translated to ϕ in the actual correction), normalizing to the first measurement and superimposing a spherical correction, assuming a radius that is the average of the three most prominent directions of crystal development. Both structures were solved by standard Patterson and Fourier methods.

Refinements were carried out on all observed reflections by using full matrix refinements (LANL system of X-ray codes [8]) with a calculated secondary extinction correction [11], corrections for neutral atom scattering factors [9] and anomalous scattering [10] (f' and f'') for all atoms. All atoms heavier than hydrogen were refined anisotropically. Although peaks appeared in the final difference Fourier map that could be interpreted in terms of hydrogen atoms, no attempt was made to include them in the refinements. For $UO_2(bmppt)_2(dmso)\cdot$acetone two peaks appeared in the difference Fourier maps in positions that were reasonable for the sulfur atom of the coordinated dmso ligand. These were both assigned as sulfur and population factors were refined (S(2) and S(3) in Tables III, V (see later) and IIIs*). The population factors converged to values that summed approximately to unity (0.67 and 0.36). The other three atoms in the dmso molecule were coincident, *i.e.*, the disorder appears to be due to an umbrella vibration. In addition three large peaks (1.5–2.0 e/Å^3) appeared in the difference Fourier map that were too far removed from other atoms in the structure to be considered noise. The distances between these peaks were reasonable for C–C distances, but the angle about the central peak was 92.2°. No attempt was made to include these peaks in the refinement. Notice that the spectroscopic results (*vide supra*) indicate that the crystals contain a co-crystallized acetone molecule. The final maps for $UO_2(NO_3)_2(Hbmppt)\cdot$acetone showed no alarming features. Fractional coordinates are given in Tables II and III for $UO_2(bmppt)_2(dmso)\cdot$acetone and $UO_2(NO_3)_2(Hbmppt)\cdot$acetone, respectively. Anisotropic thermal parameters are in Tables IIs and IIIs.

Results and Discussion

$UO_2(NO_3)_2(Hbmppt)\cdot$acetone

Uranyl nitrate and Hbmpp react in ethanol in a 1:2 mole ratio to give a good yield of $UO_2(bmpp)_2\cdot$2EtOH. The analogous reaction with Hbmppt appears to give a mixture of products unless a base is used to drive the equilibrium to complexes of the type $UO_2(bmppt)_2L$. From the less polar, aprotic solvents diethyl ether or acetone the complexes $UO_2(NO_3)_2$-L·S (L = Hbmpp or Hbmppt, S = Et_2O or acetone) were obtained. These nitrate complexes are insoluble except in solvents in which they react to give other species. The ^1H NMR spectra of the solutions were useful for indicating the environment of the organic ligand. Thus, $UO_2(NO_3)_2(Hbmpp)\cdot$acetone dissolves

TABLE II. Fractional Coordinates and Thermal Parameters for $UO_2(NO_3)_2(Hbmppt)\cdot$acetone

Atom	*x*	*y*	*z*	*B*[a]	Atom	*x*	*y*	*z*	*B*
U(1)	0.25625(4)	0.45455(3)	0.17016(3)	3.25	O(1)	0.3909(7)	0.5444(6)	0.1148(6)	5.1
O(2)	0.1205(7)	0.3647(6)	0.2294(6)	4.6	O(3)	0.0785(9)	0.6102(7)	0.4798(7)	7.0
O(4)	0.2826(7)	0.4111(5)	−0.0231(6)	3.7	C(1)	0.136(1)	0.650(1)	−0.094(1)	3.2
C(2)	0.269(1)	0.636(1)	−0.286(1)	3.9	C(3)	0.235(1)	0.570(1)	−0.171(1)	2.9
C(4)	0.283(1)	0.444(1)	−0.130(1)	3.4	N(1)	0.108(1)	0.757(1)	−0.163(1)	3.4
N(2)	0.191(1)	0.747(1)	−0.280(1)	3.4	C(5)	0.325(1)	0.351(1)	0.209(1)	3.5
C(6)	0.422(1)	0.247(1)	−0.180(1)	4.7	C(7)	0.449(1)	0.150(1)	−0.245(1)	6.5
C(8)	0.382(2)	0.162(1)	−0.339(1)	6.8	C(9)	0.288(1)	0.267(1)	−0.366(1)	6.0
C(10)	0.257(1)	0.363(1)	−0.300(1)	4.1	C(11)	0.376(1)	0.607(1)	−0.401(1)	4.1
S(1)	0.0561(3)	0.6300(2)	0.0569(2)	3.5	C(12)	0.010(1)	0.867(1)	−0.136(1)	3.2
C(13)	−0.137(1)	0.866(1)	−0.079(1)	4.1	C(14)	−0.229(1)	0.976(1)	−0.056(1)	5.0
C(15)	−0.172(1)	1.083(1)	−0.091(1)	5.9	C(16)	−0.025(1)	1.081(1)	−0.149(1)	5.1
C(17)	0.069(1)	0.973(1)	−0.172(1)	4.7	O(5)	0.2437(8)	0.4801(7)	0.3768(6)	5.5
N(3)	0.136(1)	0.568(1)	0.388(1)	5.2	O(6)	0.0906(8)	0.6082(6)	0.2948(6)	5.2
O(7)	0.4260(8)	0.3080(7)	0.2774(7)	6.4	N(4)	0.486(1)	0.238(1)	0.200(1)	5.2
O(8)	0.5756(10)	0.1501(7)	0.2156(8)	8.1	O(9)	0.4387(8)	0.2674(6)	0.1082(7)	5.7
O(10)	0.7732(11)	0.0554(7)	0.4480(7)	7.9	C(18)	0.796(1)	0.031(1)	0.545(1)	6.2
C(19)	0.842(2)	0.122(1)	0.593(1)	10.7	C(20)	0.776(2)	−0.092(1)	0.618(1)	9.2

[a] $(u_{11} + u_{22} + u_{33})/3$, anisotropic thermal parameters are available as Supplementary Data.

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*Tables designated by 's' are 'Supplementary Material'.

TABLE III. Fractional Coordinates for $UO_2(bmppt)_2(dmso)\cdot$acetone[a]

Atom	x	y	z	Atom	x	y	z
U(1)	0.15617(6)	0.18447(8)	0.12215(4)	O(1)	0.128(1)	0.175(1)	0.045(1)
O(2)	0.188(1)	0.194(1)	0.198(1)	O(3)	0.299(1)	0.185(2)	0.107(1)
C(1)	0.349(2)	0.229(2)	0.082(1)	C(2)	0.433(1)	0.165(2)	0.081(1)
C(3)	0.425(2)	0.038(2)	0.079(1)	C(4)	0.499(2)	−0.034(3)	0.087(2)
C(5)	0.578(3)	0.030(5)	0.091(2)	C(6)	0.584(2)	0.155(4)	0.091(1)
C(7)	0.509(1)	0.224(3)	0.087(1)	C(8)	0.334(1)	0.343(2)	0.049(1)
C(9)	0.269(1)	0.429(2)	0.061(1)	N(1)	0.271(1)	0.520(2)	0.021(1)
N(2)	0.333(1)	0.504(2)	−0.014(1)	C(10)	0.370(1)	0.396(2)	0.001(1)
C(11)	0.439(2)	0.352(3)	−0.035(1)	C(12)	0.221(1)	0.627(2)	0.013(1)
C(13)	0.259(2)	0.738(3)	0.010(1)	C(14)	0.209(2)	0.842(3)	0.002(1)
C(15)	0.124(2)	0.831(3)	0.002(1)	C(16)	0.085(2)	0.720(3)	0.002(1)
C(17)	0.133(2)	0.617(3)	0.007(1)	S(1)	0.2071(4)	0.4286(6)	0.1126(3)
O(4)	0.197(1)	−0.021(1)	0.131(1)	S(2)	0.2646(14)	−0.1050(18)	0.1537(12)
S(3)	0.2188(8)	−0.0949(9)	0.1892(5)	C(18)	0.322(2)	−0.054(3)	0.218(1)
C(19)	0.223(2)	−0.242(3)	0.164(1)	O(5)	0.044(1)	0.308(1)	0.133(1)
C(20)	−0.022(2)	0.332(2)	0.152(1)	C(21)	−0.085(1)	0.247(2)	0.154(1)
C(22)	−0.173(1)	0.263(2)	0.159(1)	N(3)	−0.212(1)	0.157(2)	0.155(1)
N(4)	−0.150(1)	0.072(2)	0.149(1)	C(23)	−0.073(1)	0.120(2)	0.147(1)
S(4)	0.0132(4)	0.0344(6)	0.1392(3)	C(24)	−0.179(1)	−0.049(2)	0.144(1)
C(25)	−0.166(1)	−0.123(2)	0.096(1)	C(26)	−0.202(2)	−0.242(3)	0.094(1)
C(27)	−0.246(2)	−0.268(4)	0.148(2)	C(28)	−0.251(3)	−0.201(5)	0.190(2)
C(29)	−0.222(2)	−0.088(3)	0.191(1)	C(30)	−0.225(1)	0.376(2)	0.162(1)
C(31)	−0.027(1)	0.458(2)	0.176(1)	C(32)	−0.055(2)	0.476(3)	0.232(1)
C(33)	−0.051(3)	0.588(4)	0.254(2)	C(34)	−0.033(2)	0.693(5)	0.221(2)
C(35)	−0.007(2)	0.682(3)	0.167(2)	C(36)	−0.003(1)	0.553(2)	0.140(1)

[a]Anisotropic thermal parameters are available as Supplementary Data.

in dmso to give mainly $UO_2(bmpp)_2(dmso)$ and free Hbmpp and in ethanol to yield $UO_2(bmpp)_2\cdot 2ETOH$. The $UO_2(NO_3)_2(Hbmppt)\cdot$acetone complex dissolves in dmso to give free HBmppt and in ethanol to yield a mixture of free and complexed ligand. The nitrate complexes appear to represent a relatively insoluble and probably minor component present in the reaction solution. However, they may well be intermediates along the reaction pathway that yields complexes of the type $UO_2(bmppt)_2L$.

An ORTEP projection of the molecular structure of $UO_2(NO_3)_2(Hbmppt)\cdot$acetone is shown in Fig. 1. Selected bond distances and angles are presented in Table IV. The equatorial plane of the uranyl cation is occupied by an approximately planar set of one sulfur and five oxygen atoms provided by two bidentate nitrate anions and the bidentate Hbmppt ligand. Deviations of the inner coordination sphere atoms from the least squares equatorial plane are less than 0.07 Å. The seven oxygens and one sulfur form an irregular hexagonal bipyramid about the uranium which is similar to the coordination polyhedra in $UO_2(NO_3)_2L_2$ (L = trimethylphosphate [12], triethylphosphate [13], tri-i-butyl phosphate [14], ti-n-butylphosphine oxide [15], triphenylphosphine oxide [16], triphenylarsine oxide [17], (2-nitrophenyl)diphenylphosphine oxide [18], H_2O [19, 20], and ethyl carbamate [21] and in $UO_2(NO_3)_2L$ (L = neutral bidentate CMP ligand: $R_2P(O)CH_2C(O)N(C_2H_5)_2$; R = $i\text{-}C_3H_7O$ [22]; R = C_6H_5 [23]; R_2 = $(C_6H_5)(C_2H_5O)$ [23]).

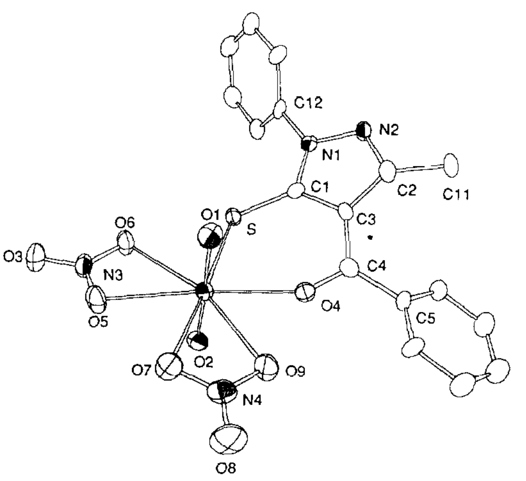


Fig. 1. Molecular structure of $UO_2(NO_3)_2(Hbmppt)\cdot$acetone.

A remarkable feature of the structure is the dihedral angle of 36.3° between the equatorial plane of the uranyl cation and the least squares plane of the Hbmppt ligand. The near coplanarity (*vide infra*) of the thiopyrazolone moiety and the acyl carbonyl and the bond distances and angles in these groups

TABLE IV. Selected Distances (Å) and Angles (°) for UO$_2$(NO$_3$)$_2$(Hbmppt)·acetone

U–O(1)	1.741(6)	U–O(6)	2.490(7)
U–O(2)	1.752(6)	U–O(7)	2.496(7)
U–O(4)	2.365(7)	U–O(9)	2.529(7)
U–O(5)	2.484(7)	U–S(1)	2.871(3)
C(1)–S(1)	1.706(9)	N(3)–O(3)	1.21(1)
C(1)–C(3)	1.41(1)	N(3)–O(5)	1.27(1)
C(1)–N(1)	1.35(1)	N(3)–O(6)	1.26(1)
C(2)–C(3)	1.40(1)	N(4)–O(7)	1.26(1)
C(2)–C(11)	1.50(1)	N(4)–O(8)	1.20(1)
C(2)–N(2)	1.34(1)	N(4)–O(9)	1.25(1)
C(3)–C(4)	1.45(1)	C(18)–C(19)	1.49(2)
C(4)–C(5)	1.47(1)	C(18)–C(20)	1.52(2)
C(4)–O(4)	1.24(1)	C(18)–O(10)	1.20(1)
N(1)–N(2)	1.38(1)	N(2)···O(10)	2.71(1)
N(1)–C(12)	1.43(1)	N(2)···O(8)	3.12(1)
Angles about uranium and inner coordination sphere atoms			
O(1)–U–O(2)	178.6(3)	O(4)–U–S(1)	70.1(2)
O(1)–U–O(4)	92.0(3)	O(5)–U–O(6)	50.8(2)
O(1)–U–O(5)	89.2(3)	O(5)–U–O(7)	61.6(2)
O(1)–U–O(6)	91.3(3)	O(5)–U–O(9)	111.1(2)
O(1)–U–O(7)	88.6(3)	O(5)–U–S(1)	115.5(2)
O(1)–U–O(9)	92.4(3)	O(6)–U–O(7)	112.4(2)
O(1)–U–S(1)	91.1(2)	O(6)–U–O(9)	161.5(2)
O(2)–U–O(4)	89.5(3)	O(6)–U–S(1)	64.6(2)
O(2)–U–O(5)	89.4(3)	O(7)–U–O(9)	49.6(2)
O(2)–U–O(6)	87.8(3)	O(7)–U–S(1)	177.1(2)
O(2)–U–O(7)	90.8(3)	O(9)–U–S(1)	133.3(2)
O(2)–U–O(9)	88.1(3)	U–O(4)–C(4)	151.2(6)
O(2)–U–S(1)	89.4(2)	U–O(5)–N(3)	97.0(5)
O(4)–U–O(5)	174.3(2)	U–O(6)–N(3)	96.9(6)
O(4)–U–O(6)	134.7(2)	U–O(7)–N(4)	98.9(6)
O(4)–U–O(7)	112.8(2)	U–O(9)–N(4)	97.4(6)
O(4)–U–O(9)	63.3(2)	U–S(1)–C(1)	108.3(3)
Ligand angles			
O(3)–N(3)–O(5)	123.0(9)	N(2)–C(2)–C(3)	107.6(8)
O(3)–N(3)–O(6)	122(1)	N(2)–C(2)–C(11)	119.0(8)
O(5)–N(3)–O(6)	115.1(8)	C(3)–C(2)–C(11)	133.3(9)
O(7)–N(4)–O(8)	122(1)	C(1)–C(3)–C(2)	107.4(8)
O(7)–N(4)–O(9)	114.1(8)	C(1)–C(3)–C(4)	122.8(8)
O(8)–N(4)–O(9)	124(1)	C(2)–C(3)–C(4)	129.7(8)
S(1)–C(1)–N(1)	121.8(6)	C(3)–C(4)–C(5)	122.3(9)
S(1)–C(1)–C(3)	131.6(7)	C(3)–C(4)–O(4)	119.4(8)
C(3)–C(1)–N(1)	106.6(8)	O(4)–C(4)–C(5)	118.1(8)
C(1)–N(1)–N(2)	108.9(7)	O(10)–C(18)–C(19)	120(1)
C(1)–N(1)–C(12)	131.5(8)	O(10)–C(18)–C(20)	119(1)
N(2)–N(1)–C(12)	119.6(7)	C(19)–C(18)–C(20)	121(1)
N(1)–N(2)–C(2)	109.4(7)	N(2)···O(10)–C(18)	130.5(8)

indicate sp^2 hybridization of these atoms and substantial double bond character in the CS and CO groups. Thus binding of the uranium in the plane of the Hbmppt ligand would be expected to give the strongest interaction with the ligand donor orbitals. We attribute the binding of the Hbmppt ligand out of the equatorial plane to the formation of a hydrogen bond between the Hbmppt ligand in its N–H tautomeric form and the acetone of crystallization. The N(1)–O(10) distance of 2.71(1) Å is indicative of a reasonably strong hydrogen bond between the N–H group of the pyrazolone ligand and the oxygen atom of the acetone [24]. The acetone oxygen is nearly in the plane of the pyrazole ring and the acetone molecule is oriented so that a lone pair on the oxygen is approximately directed along the N(2)–O(10) axis, N(2)–O(10)–C(18) = 130.5(8)°. The existence of the hydrogen bond is confirmed by the infrared spectrum, which exhibits a ν(CO) for the acetone at 1690 cm^{-1}, a shift down from the value for free acetone at 1710 cm^{-1} (the IR spectrum of UO$_2$(bmppt)$_2$(dmso)·acetone shows a strong, sharp band assigned to ν(CO) of acetone at 1711 cm^{-1}). An N–H···acetone hydrogen bond was observed in the structure of tris(2-aminocyclopentene-1-dithiocarboxylato)Co(III)·acetone with an N···O distance of 2.99 Å and ν(CO) 1700 cm^{-1} [25]. The only other intermolecular N(2)–atom distances less than 3.5 Å are N(2)–O(8) 3.12(1) Å and N(2)–O(2) 3.39(1) Å.

The U–S(1) distance of 2.871(3) Å seems rather short for a neutral sulfur donor binding to UO$_2^{2+}$. This distance lies halfway between the U–S distances found in UO$_2$(bmppt)$_2$(dmso)·acetone (*vide infra*) of 2.836(6) and 2.902(6) Å. The average U–S distances observed for other uranyl complexes containing anionic S,S or S,O donor ligands fall in the range 2.84–2.87 Å [26–31], except for [UO$_2$(S$_2$CNEt$_2$)$_3$][NMe$_4$] with an average U–S distance of 2.80 Å [32]. Three structures of complexes were determined where a uranyl cation was bound to a thioether sulfur atom of a multidentate ligand with U–S distances of 2.94(1) [33], 2.96(1) [34], and 3.018(4) Å [35]. A clear example of the difference in bond distances between thiolate and thiol type sulfur linkages to an actinide metal center (0.27 Å) is provided by the structure of (η^5-Me$_5$C$_5$)$_2$ThS$_5$ [36]. The U–O(4) distance of 2.365(7) Å is 0.030 Å shorter than the average of the corresponding U–O acyl distances in UO$_2$(bmpp)$_2$(dmso) [7], but 0.040 Å longer than the average of the U–O(3) and U–O(5) distances in UO$_2$(bmppt)$_2$(dmso)·acetone (Fig. 2

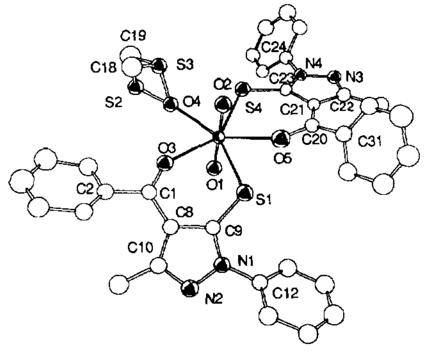
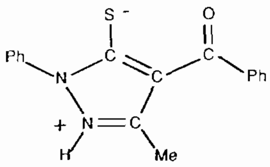


Fig. 2. Molecular structure of UO$_2$(bmppt)$_2$(dmso)·acetone.

and Table V). Taken together the U–O(4) and U–S(1) distances suggest a charge density on these atoms in the neutral Hbmppt ligand comparable to that of the anion. This can be envisioned to result from substantial contributions of the zwitterionic forms of the N–H tautomer to the electronic structure of the coordinated ligand.



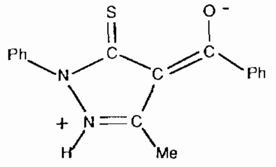


TABLE V. Selected Distances (Å) and Angles (°) for UO_2-$(bmppt)_2$(dmso)•acetone.

U–O(1)	1.77(1)	U–O(5)	2.29(2)
U–O(2)	1.76(2)	U–S(1)	2.836(6)
U–O(3)	2.36(1)	U–S(4)	2.902(6)
U–O(4)	2.37(1)		
C(1)–O(3)	1.18(3)	C(19)–S(3)	1.73(4)
C(1)–C(2)	1.52(3)	O(4)–S(2)	1.46(2)
C(1)–C(8)	1.46(3)	O(4)–S(3)	1.57(2)
C(8)–C(9)	1.47(3)	C(20)–O(5)	1.25(3)
C(8)–C(10)	1.44(3)	C(20)–C(21)	1.38(3)
C(9)–N(1)	1.37(3)	C(20–C(31)	1.50(3)
C(9)–S(1)	1.65(2)	C(21)–C(22)	1.45(3)
N(1)–C(12)	1.43(3)	C(21)–C(23)	1.43(3)
N(1)–N(2)	1.38(2)	C(22)–C(30)	1.50(3)
C(10)–N(2)	1.36(3)	C(22)–N(3)	1.33(3)
C(10)–C(11)	1.55(3)	N(3)–N(4)	1.39(2)
C(18)–S(2)	1.71(3)	N(4)–C(24)	1.42(3)
C(18)–S(3)	1.74(3)	C(23)–N(4)	1.35(3)
C(19)–S(2)	1.68(4)	C(23)–S(4)	1.71(2)
Angles about uranium and inner coordination sphere atoms			
O(1)–U–O(2)	178.2(7)	O(3)–U–S(4)	145.3(4)
O(1)–U–O(3)	87.8(7)	O(4)–U–O(5)	140.6(6)
O(1)–U–O(4)	92.8(6)	O(4)–U–S(1)	147.2(4)
O(1)–U–O(5)	93.2(7)	O(4)–U–S(4)	69.8(4)
O(1)–U–S(1)	90.8(6)	O(5)–U–S(1)	71.5(4)
O(1)–U–S(4)	90.8(6)	O(5)–U–S(4)	71.2(4)
O(2)–U–O(3)	90.4(7)	S(1)–U–S(4)	142.8(2)
O(2)–U–O(4)	86.8(6)	U–O(3)–C(1)	145(2)
O(2)–U–O(5)	88.2(8)	U–O(4)–S(2)	145(1)
O(2)–U–S(1)	88.7(5)	U–O(4)–S(3)	126.1(9)
O(2)–U–S(4)	90.7(5)	U–O(5)–C(20)	153(2)
O(3)–U–O(4)	75.6(5)	U–S(1)–C(9)	105.7(8)
O(3)–U–O(5)	143.5(6)	U–S(4)–C(23)	111.4(8)
O(3)–U–S(1)	72.0(4)		
Ligand angles			
C(2)–C(1)–O(3)	119(2)	C(31)–C(20)–O(5)	116(2)
C(2)–C(1)–C(8)	118(2)	C(31)–C(20)–C(21)	123(2)
C(8)–C(1)–O(3)	123(2)	C(21)–C(20)–O(5)	122(2)
C(1)–C(8)–C(9)	122(2)	C(20)–C(21)–C(23)	124(2)
C(1)–C(8)–C(10)	133(2)	C(20)–C(21)–C(22)	130(2)
C(9)–C(8)–C(10)	105(2)	C(23)–C(21)–C(22)	106(2)
C(8)–C(10)–C(11)	133(2)	C(21)–C(22)–C(30)	131(2)
C(8)–C(10)–N(2)	110(2)	C(21)–C(22)–N(3)	110(2)
C(11)–C(10)–N(2)	117(2)	C(30)–C(22)–N(3)	119(2)
C(10)–N(2)–N(1)	106(2)	C(22)–N(3)–N(4)	106(2)
C(9)–N(1)–N(2)	114(2)	C(23)–N(4)–N(3)	114(2)
C(9)–N(1)–C(12)	129(2)	C(23)–N(4)–C(24)	131(2)
C(12)–N(1)–N(2)	118(2)	C(24)–N(4)–N(3)	115(2)
C(8)–C(9)–N(1)	105(2)	C(21)–C(23)–N(4)	104(2)
C(8)–C(9)–S(1)	131(2)	C(21)–C(23)–S(4)	133(2)
N(1)–C(9)–S(1)	124(2)	N(4)–C(23)–S(4)	123(2)
C(18)–S(2)–O(4)	112(2)	C(18)–S(3)–O(4)	105(1)
C(18)–S(2)–C(19)	110(2)	C(18)–S(3)–C(19)	107(2)
C(19)–S(2)–O(4)	110(2)	C(19)–S(3)–O(4)	102(1)

The nitrate ions are nearly coplanar with the uranyl equatorial plane with dihedral angles of 3.5° and 7.0°. The U–O distances to the nitrate oxygens range from 2.484(7) to 2.529(7) Å and are quite similar to those found in, e.g., the $UO_2(NO_3)_2$-(CMP) structures [22, 23].

UO_2(bmppt)(dmso)•acetone

An ORTEP projection of the molecular structure of $UO_2(bmppt)_2$(dmso)•acetone is shown in Fig. 2. Selected bond distances and angles are presented in Table V. The crystal contains discrete molecules of $UO_2(bmppt)_2$(dmso) with the uranyl ion bound to two bidentate acyl thiopyrazolone anions and a neutral dmso molecule in the equatorial plane. Deviations of these five donor atoms from the least squares equatorial plane are less than 0.09 Å. The five oxygen and two sulfur atoms form an irregular pentagonal bipyramid about the uranium. Many structures have been determined that exhibit this pentagonal bipyramidal geometry with two 1,3-dionate ligands and a variety of monodentate ligands in the uranyl equatorial plane (see ref. 7 and references therein).

In contrast to the 1,3-dionate structures referred to above, including that of $UO_2(bmpp)_2$(dmso) [7], the bmppt anions in $UO_2(bmppt)_2$(dmso) are bound quite unsymmetrically to the uranium atom. The dihedral angle between bmppt anion(1) and the uranyl equatorial plane is 38.5°, whereas anion(2) is more nearly coplanar (11.0°). Anion(1) has a short U–S(1) distance (2.836(6) Å) and a long U–O(3) distance (2.355(15) Å) relative to anion(2) (2.902(6) and 2.293(16) Å although the difference in U–O distances 0.062(22) Å is barely 3σ. Variations in C–O, C–S, and C–C bond lengths that might indicate differences in the π bonding systems of the anions are within experimental error. There is no readily discernible cause for the large dihedral angle for anion(1). No intermolecular contacts, such as the hydrogen bonding found in $UO_2(NO_3)_2$-(Hbmppt)•acetone (*vide supra*), are present that might explain such a feature. Dihedral angles between the 1,3-dionate plane and the uranyl equatorial plane of greater than 20° have been observed in three structures: UO_2(3-Clacac)$_2$(Ph_3PO) (23, 2°) [37], $UO_2(hfacac)_2[(CH_3O)_3PO]$ (22.5, 22.5°) [38], and

$UO_2(thd)_2(CH_3OH)$ (29.1, 14.5°) [39] (3-Clacac = 3-chloropentane-2,4-dionate, hfacac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate, thd = 2,2,6,6-tetramethylheptane-3,5-dionate). The latter two structures have been described as having a 'boat' configuration with both 1,3-dionate ligands folded toward the same side of the equatorial plane. Again, there are no obvious explanations for the deviations from planarity in these complexes. The largely ionic bonding in these complexes apparently allows considerable flexibility in the dihedral angle, which can be influenced by subtle intramolecular and intermolecular forces.

The average of the U–S distances, 2.869 Å, falls in the range (2.84–2.87 Å) observed for other uranyl complexes with two bidentate anions with S,S or S,O donor atoms [26–31]. Note that in the $UO_2[Et_2NC(O)S]_2(OEt)^-$ anion [28] and UO_2(1-oxo-2-thiopyridinato)$_2$(dmso) [26] the S,O donor anions do not show any significant differences in their binding to the uranyl cation. The average U–O distance of 2.324 Å in UO_2(bmppt)$_2$(dmso) is considerably shorter than the average for the corresponding U–O acyl oxygen distances in UO_2(bmpp)$_2$(dmso) of 2.395 Å. Again, this indicates a greater charge density on the acyl oxygen in the bmppt anion relative to the bmpp anion presumably caused by the substitution of oxygen with the less electronegative sulfur atom. A similar effect was seen in comparing the structures of UO_2(1-oxo-2-thiopyridinato)$_2$(dmso) and UO_2(1,2-dioxopyridinato)$_2$(H_2O) [26].

In both structures, significant deviations of the acyl C and O atoms from the least squares plane of the pyrazalone ring are observed. These displacements are: $UO_2(NO_3)_2$(Hbmppt)·acetone, C(4), −0.105 Å; O(4), 0.305 Å; UO_2(bmppt)$_2$dmso·acetone; C(1), 0.056 Å, O(3), 0.443 Å, C(20), 0.074 Å, O(5), 0.421 Å. These distortions may alternatively be described in terms of the dihedral angles between the pyrazalone plane and the plane defined by the acyl C,O atoms and the C atom to which it is bonded in the pyrazalone ring of 24.6, 21.5, and 18.5°, respectively. The deviation from coplanarity is clearly dictated by steric factors; e.g., for $UO_2(NO_3)_2$(Hbmppt)·acetone the S–O distance in the Hbmppt ligand is 3.034 Å compared to a van der Waals distance of 3.25 Å.

The dmso molecule occupying the fifth equatorial coordination site is disordered, and the two partially occupied sulfur positions are shown in Fig. 2. The U–O(5) distance of 2.365(15) Å can be compared to the U–O(dmso) distances of 2.32(2) Å in UO_2(1-oxo-2-thiopyridinato)$_2$(dmso) [26] and 2.378(7) Å in UO_2(bmpp)$_2$(dmso) [7] indicating a greater overall binding strength to UO_2^{2+} for the bmppt anion than for 1-oxo-2-thiopyridinato and comparable to the bmpp anion.

Further work is in progress to define the coordination chemistry of Hbmppt and other sulfur donor ligands with the actinides and lanthanides. Initial solvent extraction studies using Hbmppt in benzene with trioctylphosphine oxide as a synergist have shown interesting selectivity properties, e.g., preferential extraction of Am^{3+} over Eu^{3+} [40]. These results suggest that sulfur donor ligands will indeed have coordination properties useful for analysis and separation of the actinides.

Supplementary Material

Anisotropic thermal parameters (Tables IIs and IIIs) are available from the authors on request.

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