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# Sulfonate Complexes of Actinide Ions: Structural Diversity in Uranyl Complexes with 2-Sulfobenzoate

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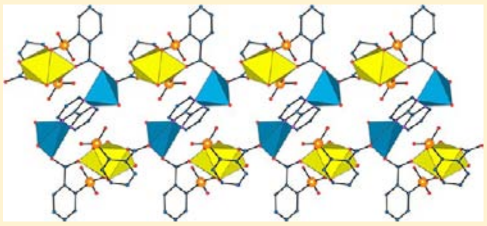
*Supporting Information*



**ABSTRACT:** The reaction of uranyl nitrate hexahydrate with 2-sulfobenzoate ($SB^{2-}$) in the presence of various amines gave the series of complexes $[UO_2(SB)(H_2O)]$ (**1**), $[UO_2(SB)(H_2O)]_2{\cdot}pyz$ (**2**), $[2,2'\text{-bipyH}]_2[UO_2(SB)_2(H_2O)]{\cdot}4H_2O$ (**3**), $[4,4'\text{-bipyH}_2]_2[UO_2(SB)_2]_2$ (**4**), $[4,4'\text{-bipyH}]_2[(UO_2)_2(SB)_3(H_2O)]{\cdot}4H_2O$ (**5**), $[NMe_4]_2[(UO_2)_2(SB)_3(H_2O)_{1.15}]{\cdot}1.35H_2O$ (**6**), $[NMe_4]_2[(UO_2)_3(SB)_2O_2]$ (**7**), and $[H_2DABCO]_2[(UO_2)_5(SB)_4O_2(OH)_2]{\cdot}4H_2O$ (**8**), where pyz = pyrazine, bipy = bipyridine, and DABCO = 1,4-diazabicyclo[2.2.2]octane, with all compounds but **5** having been obtained under hydrothermal conditions. The crystal structures of these complexes display a common motif in which uranyl is chelated by the carboxylate and sulfonate groups of SB, giving a seven-membered ring. Structure-directing effects due to the amine and the presence in **7** and **8** of additional $\mu_3$-oxo or $\mu_2$-hydroxo bridges result in much structural variety, with different bridging by the carboxylate and sulfonate groups giving rise to zero- (**3**, **4**), one- (**1**, **5**−**8**), or two-dimensional (**2**) assemblies. Some unusual uranyl secondary building units are observed, such as the pentanuclear $[(UO_2)_5O_2(OH)_2]$ discrete motif. Addition of 3d-block metal cations ($Cu^{2+}$, $Ni^{2+}$) in the presence of nitrogen donors gave the heterometallic molecular complex $[UO_2Cu(SB)_2(2,2'\text{-bipy})_2]_2{\cdot}2H_2O$ (**9**), the heterogeneous compound $[Cu(4,4'\text{-bipy})(H_2O)_3]_2[UO_2(SB)_2]_2{\cdot}2H_2O$ (**10**), in which molecular uranyl dimers are encompassing copper-containing chains, and the heterometallic one-dimensional polymers $[(UO_2)_2Cu_2(SB)_4(\text{bipym})(H_2O)_4]$ (**11**) and $[UO_2Ni(SB)_2(\text{bipym})(H_2O)_2]{\cdot}3H_2O$ (**12**), where bipym = bipyrimidine. The latter two complexes display two different arrangements: in **11**, bipym bridges two $[UO_2Cu(SB)_2]$ chains to give a ladderlike assembly, while the uranyl cations are merely decorating species in **12**. In contrast to those of phosphonates, the actinide complexes of sulfonates in the solid state have been little investigated up to now. The present results show that sulfocarboxylates such as 2-sulfobenzoate, in which sulfonate coordination is promoted by chelate effects, are of interest in the synthesis of uranyl−organic coordination polymers.

## ■ INTRODUCTION

In the past years, phosphonates have become a prominent family of ligands among those used in the synthesis of uranyl−organic frameworks (UOFs), which are most commonly built from polycarboxylates.[1] Several groups have exploited the high affinity of phosphonic acids for uranyl to generate a large array of original architectures, from one-dimensional nanotubules up to three-dimensional frameworks,[2] in keeping with the richness of phosphonate structural chemistry in the more encompassing field of metal−organic frameworks.[3] In contrast, and although they are geometrically similar to phosphonates, sulfonates are weaker ligands (one obvious difference being their lower charge compared with fully deprotonated phosphonates) and they have been much less used in the design of metal−organic species.[4] However, examples of extended architectures involving sulfonates have been reported with alkali, alkaline-earth, d-block, and 4f metal cations.[4,5] In the particular case of actinide ions, most of the sulfonate complexes reported in the Cambridge Structural Database (CSD, Version 5.33)[6] involve the very common trifluoromethanesulfonate anion, which is found as a bridging ligand in some remarkable structures, such as polyoxo uranium clusters.[7] Several extended structures, one- or two-dimensional, have been obtained with uranyl cations and bridging bidentate methane- and ethanesulfonate anions,[8] while trifluoromethanesulfonate was reported to give a linear coordination polymer with uranium(III).[9] More recently, 1,2-ethanedisulfonic, 2-, 3-, and 4-sulfobenzoic, and 4,5-dihydroxy-1,3-benzenedisulfonic acids were used as coligands in uranyl complexes with cucurbit[6]uril,[10] and the former appeared suitable for the synthesis of one-dimensional mixed uranyl−lanthanide complexes.[11] Two-dimensional uranyl and uranyl−lanthanide assemblies with *p*-sulfonatocalix[4]arene were also described.[12] Uranyl coordination by sulfonates is also of environmental relevance, due to the presence of sulfonate groups in humic substances, although in low concentration.[13] Finally, two thorium(IV) molecular species containing the trifluoromethanesulfonate anion have also been described.[14] It appears clearly that the potential of sulfonates in the synthesis of uranyl−organic coordination polymers has been underexploited, and the present work is aimed at exploring the behavior of one such molecule, 2-sulfobenzoate (the dianionic form of which will be denoted SB in the following), which proved suitable to get uranyl complexes in single crystal form, mainly under mild hydrothermal conditions

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and in the presence of various additional reagents. A series of eight complexes was thus obtained in the presence of different organic bases, $NMe_4OH$, pyrazine (pyz), 2,2′- and 4,4′-bipyridine (2,2′- and 4,4′-bipy), and 1,4-diazabicyclo[2.2.2]octane (DABCO), which induce large variations in the dimensionality and geometry of the complexes formed. A second series of four complexes contain an additional 3d-block metal cation ($Cu^{2+}$ or $Ni^{2+}$), and 2,2′-bipy, 4,4′-bipy, or bipyrimidine (bipym) coligands.

## ■ EXPERIMENTAL SECTION

**Synthesis.** *Caution! Uranium is a radioactive and chemically toxic element, and uranium-containing samples must be handled with suitable care and protection.*

$UO_2(NO_3)_2\cdot6H_2O$ (depleted uranium, R. P. Normapur, 99%) and $Ni(NO_3)_2\cdot6H_2O$ (99%) were purchased from Prolabo, $Cu(NO_3)_2\cdot2.5H_2O$ (98%) and 2-sulfobenzoic acid cyclic anhydride were from Sigma-Aldrich, and the other reagents were from Aldrich, Acros, or Fluka. Elemental analyses were performed by MEDAC Ltd. at Chobham, U.K.

**$[UO_2(SB)(H_2O)]$ (1).** 2-Sulfobenzoic acid cyclic anhydride (SBAn, 19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), 2-aminopyridine (10 mg, 0.11 mmol), and demineralized water (1 mL) were placed in a 10 mL tightly closed glass vessel. Light yellow crystals of complex **1** appeared in low yield upon heating the solution at 180 °C under autogenous pressure for one month. This complex was also obtained without a base, from uranyl sulfate or trifluoromethanesulfonate instead of nitrate.

**$[UO_2(SB)(H_2O)]_2\cdot pyz$ (2).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), pyrazine (16 mg, 0.20 mmol), and demineralized water (1 mL) were placed in a 10 mL tightly closed glass vessel. Light yellow crystals of complex **2** appeared in low yield upon heating the solution at 180 °C under autogenous pressure for one week. The yield was not improved upon prolonged heating.

**$[2,2'\text{-bipyH}]_2[UO_2(SB)_2(H_2O)]\cdot4H_2O$ (3).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), 2,2′-bipyridine (16 mg, 0.10 mmol), and demineralized water (1 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure for one month, yielding light yellow crystals of complex **3** upon cooling down (20 mg, 37% yield on the basis of SB). Anal. Calcd for $C_{34}H_{36}N_4O_{17}S_2U$: C, 37.99; H, 3.38; N, 5.21; S, 5.97. Found: C, 38.57; H, 3.30; N, 5.24; S, 5.81%.

**$[4,4'\text{-bipyH}_2]_2[UO_2(SB)_2]_2$ (4).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), 4,4′-bipyridine (16 mg, 0.10 mmol), and demineralized water (1 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure for one month, yielding light yellow crystals of complex **4** in low yield upon cooling down.

**$[4,4'\text{-bipyH}]_2[(UO_2)_2(SB)_3(H_2O)]\cdot4H_2O$ (5).** SBAn (38 mg, 0.20 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (100 mg, 0.20 mmol) and 4,4′-bipyridine (32 mg, 0.20 mmol) were dissolved in demineralized water (1.4 mL), and the solution was allowed to slowly evaporate, yielding light yellow crystals of complex **5** within one month, mixed with large, colorless crystals of $(4,4'\text{-bipyH}_2)(NO_3)_2$, which were separated manually after filtration. For **5**: 29 mg, 28% yield on the basis of SB. Anal. Calcd for $C_{41}H_{40}N_4O_{24}S_3U_2$: C, 31.87; H, 2.61; N, 3.63; S, 6.23. Found: C, 31.86; H, 2.43; N, 3.83; S, 5.89%.

**$[NMe_4]_2[(UO_2)_2(SB)_3(H_2O)_{1.15}]\cdot1.35H_2O$ (6).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), $NMe_4OH\cdot5H_2O$ (36 mg, 0.20 mmol), and demineralized water (1 mL) were placed in a 10 mL tightly closed glass vessel. Light yellow crystals of complex **6** appeared in low yield upon heating the solution at 180 °C under autogenous pressure for two weeks. The yield was not improved upon prolonged heating.

**$[NMe_4]_2[(UO_2)_3(SB)_2O_2]$ (7).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), $Cu(NO_3)_2\cdot2.5H_2O$ (23 mg, 0.10 mmol), $NMe_4OH\cdot5H_2O$ (36 mg, 0.20 mmol), and demineralized water (1 mL) were placed in a 10 mL tightly closed glass vessel. Light yellow crystals of complex **7** appeared in low yield upon heating the solution at 180 °C under autogenous pressure for one month.

**$[H_2DABCO]_2[(UO_2)_5(SB)_4O_2(OH)_2]\cdot4H_2O$ (8).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), DABCO (22 mg, 0.20 mmol), and demineralized water (1 mL) were placed in a 10 mL tightly closed glass vessel. Light yellow crystals of complex **8** were deposited in low yield upon heating the solution at 180 °C under autogenous pressure for ten days. The yield was not improved upon prolonged heating.

**$[UO_2Cu(SB)_2(2,2'\text{-bipy})_2]_2\cdot2H_2O$ (9).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), $Cu(NO_3)_2\cdot2.5H_2O$ (23 mg, 0.10 mmol), 2,2′-bipyridine (32 mg, 0.20 mmol), and demineralized water (1.5 mL) were placed in a 10 mL tightly closed glass vessel. Light blue-green crystals of complex **9** were deposited upon heating the solution at 180 °C under autogenous pressure for three days (8 mg, 15% yield on the basis of SB). Anal. Calcd for $C_{68}H_{52}Cu_2N_8O_{26}S_4U_2$: C, 38.37; H, 2.46; N, 5.26; S, 6.03. Found: C, 38.31; H, 2.49; N, 5.18; S, 5.85%.

**$[Cu(4,4'\text{-bipy})(H_2O)_3]_2[UO_2(SB)_2]_2\cdot2H_2O$ (10).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), $Cu(NO_3)_2\cdot2.5H_2O$ (23 mg, 0.10 mmol), 4,4′-bipyridine (16 mg, 0.10 mmol), and demineralized water (1.5 mL) were placed in a 10 mL tightly closed glass vessel. Light green crystals of complex **10** were deposited upon heating the solution at 180 °C under autogenous pressure for three days (6 mg, 12% yield on the basis of SB). Anal. Calcd for $C_{48}H_{48}Cu_2N_4O_{32}S_4U_2$: C, 29.96; H, 2.51; N, 2.91; S, 6.67. Found: C, 30.21; H, 2.62; N, 2.82; S, 6.27%.

**$[(UO_2)_2Cu_2(SB)_4(bipym)(H_2O)_4]$ (11).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), $Cu(NO_3)_2\cdot2.5H_2O$ (23 mg, 0.10 mmol), 2,2′-bipyrimidine (16 mg, 0.10 mmol), and demineralized water (1.5 mL) were placed in a 10 mL tightly closed glass vessel. Light green crystals of complex **11** were deposited in very low yield upon heating the solution at 180 °C under autogenous pressure for three weeks.

**$[UO_2Ni(SB)_2(bipym)(H_2O)_2]\cdot3H_2O$ (12).** SBAn (19 mg, 0.10 mmol), $UO_2(NO_3)_2\cdot6H_2O$ (50 mg, 0.10 mmol), $Ni(NO_3)_2\cdot6H_2O$ (30 mg, 0.10 mmol), 2,2′-bipyrimidine (16 mg, 0.10 mmol), and demineralized water (1.5 mL) were placed in a 10 mL tightly closed glass vessel. Light green crystals of complex **12** were deposited in very low yield upon heating the solution at 180 °C under autogenous pressure for three weeks.

**Crystallography.** The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[15] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames and then refined on all data. The data (combinations of $\varphi$- and $\omega$-scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[16] Absorption effects were corrected empirically with the program SCALEPACK.[16] The structures were solved by direct methods or Patterson map interpretation with SHELXS-97, expanded by subsequent Fourier-difference synthesis, and refined by full-matrix least-squares on $F^2$ with SHELXL-97.[17] All non-hydrogen atoms were refined with anisotropic displacement parameters, with restraints for some atoms in the disordered parts and/or for some solvent water molecules, when present. Some lattice water molecules were given partial occupancy factors in order to retain acceptable displacement parameters and/or to account for too close contacts. Most hydrogen atoms bound to oxygen and nitrogen atoms were found on Fourier-difference maps (see details below), except for those of some solvent water molecules, and the carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for $CH_3$). Special details are as follows.

**Compound 3.** The SB molecule is disordered over two positions sharing the aromatic ring and four oxygen atoms, the carboxylate group of one position being superimposed to the sulfonate of the other; these two positions were refined with occupancy parameters constrained to sum to unity. One solvent water molecule (O9) is also disordered over two positions (sharing the same hydrogen atoms), which were refined with occupancy parameters constrained to sum to

Table 1. Crystal Data and Structure Refinement Details

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| chem formula | $C_7H_6O_8SU$ | $C_{18}H_{16}N_2O_{16}S_2U_2$ | $C_{34}H_{36}N_4O_{17}S_2U$ | $C_{48}H_{36}N_4O_{24}S_4U_2$ | $C_{41}H_{40}N_4O_{24}S_3U_2$ | $C_{29}H_{41}N_2O_{21.5}S_3U_2$ |
| $M$ (g mol$^{-1}$) | 488.21 | 1056.50 | 1074.82 | 1657.11 | 1545.01 | 1333.88 |
| cryst syst | orthorhombic | monoclinic | monoclinic | monoclinic | monoclinic | triclinic |
| space group | $Pbcn$ | $P2_1/c$ | $C2/c$ | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ |
| $a$ (Å) | 20.8194(5) | 7.8894(4) | 24.4982(3) | 10.7449(3) | 10.743(4) | 14.8569(7) |
| $b$ (Å) | 7.8416(2) | 12.0629(4) | 9.9823(2) | 23.4648(10) | 32.178(2) | 16.3899(7) |
| $c$ (Å) | 13.0646(3) | 13.3182(7) | 18.6719(3) | 10.1872(4) | 14.3508(10) | 20.0779(8) |
| $\alpha$ (deg) | 90 | 90 | 90 | 90 | 90 | 88.442(3) |
| $\beta$ (deg) | 90 | 94.573(3) | 122.1545(9) | 95.448(3) | 100.324(4) | 70.273(2) |
| $\gamma$ (deg) | 90 | 90 | 90 | 90 | 90 | 66.815(2) |
| $V$ (Å$^3$) | 2132.89(9) | 1263.45(10) | 3865.80(12) | 2556.87(16) | 4880.6(19) | 4198.8(3) |
| $Z$ | 8 | 2 | 4 | 2 | 4 | 4 |
| $D_{calcd}$ (g cm$^{-3}$) | 3.041 | 2.777 | 1.847 | 2.152 | 2.103 | 2.110 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 15.444 | 13.050 | 4.388 | 6.583 | 6.847 | 7.935 |
| $F$(000) | 1760 | 964 | 2112 | 1584 | 2952 | 2532 |
| reflns collcd | 66098 | 43705 | 123150 | 70906 | 66867 | 254245 |
| indep reflns | 3259 | 3858 | 5884 | 7797 | 12563 | 21671 |
| obsd reflns [$I > 2\sigma(I)$] | 2441 | 3079 | 5635 | 5560 | 6022 | 16614 |
| $R_{int}$ | 0.021 | 0.084 | 0.033 | 0.059 | 0.128 | 0.062 |
| params refined | 154 | 181 | 301 | 370 | 667 | 1101 |
| R1 | 0.026 | 0.028 | 0.027 | 0.042 | 0.077 | 0.038 |
| wR2 | 0.064 | 0.051 | 0.070 | 0.100 | 0.192 | 0.100 |
| $S$ | 0.980 | 0.948 | 1.116 | 1.028 | 0.980 | 1.042 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | −1.70 | −1.41 | −1.61 | −1.77 | −1.47 | −2.13 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.99 | 0.99 | 0.59 | 2.24 | 5.43 | 1.63 |

| | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|
| chem formula | $C_{22}H_{32}N_2O_{18}S_2U_3$ | $C_{40}H_{54}N_4O_{38}S_4U_5$ | $C_{68}H_{52}Cu_2N_8O_{26}S_4U_2$ | $C_{48}H_{48}Cu_2N_4O_{32}S_4U_2$ | $C_{36}H_{30}Cu_2N_4O_{28}S_4U_2$ | $C_{22}H_{24}N_4NiO_{17}S_2U$ |
| $M$ (g mol$^{-1}$) | 1390.71 | 2517.26 | 2128.56 | 1924.28 | 1698.02 | 977.31 |
| cryst syst | triclinic | monoclinic | triclinic | monoclinic | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $C2/c$ |
| $a$ (Å) | 7.0444(5) | 13.3465(1) | 11.1314(3) | 11.2043(2) | 9.0904(5) | 31.8326(5) |
| $b$ (Å) | 10.6214(10) | 28.5557(3) | 12.7398(5) | 15.0029(5) | 11.3426(7) | 10.7066(2) |
| $c$ (Å) | 11.5329(11) | 16.3283(2) | 13.4514(6) | 17.9274(6) | 13.3583(7) | 18.2942(3) |
| $\alpha$ (deg) | 83.349(4) | 90 | 89.413(2) | 90 | 73.018(3) | 90 |
| $\beta$ (deg) | 87.808(5) | 97.2807(5) | 88.893(3) | 96.5021(19) | 78.884(3) | 96.9464(13) |
| $\gamma$ (deg) | 80.027(5) | 90 | 64.583(2) | 90 | 67.506(2) | 90 |
| $V$ (Å$^3$) | 844.00(13) | 6172.85(11) | 1722.61(12) | 2994.16(15) | 1211.95(12) | 6189.24(18) |
| $Z$ | 1 | 4 | 1 | 2 | 1 | 8 |
| $D_{calcd}$ (g cm$^{-3}$) | 2.736 | 2.709 | 2.052 | 2.134 | 2.327 | 2.098 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 14.557 | 13.312 | 5.509 | 6.332 | 7.798 | 6.053 |
| $F$(000) | 630 | 4600 | 1030 | 1852 | 804 | 3776 |
| reflns collcd | 50398 | 207332 | 98925 | 110226 | 70984 | 147050 |
| indep reflns | 5142 | 15900 | 10516 | 9133 | 7381 | 9428 |
| obsd reflns [$I > 2\sigma(I)$] | 4075 | 13026 | 9372 | 7773 | 6574 | 8181 |
| $R_{int}$ | 0.082 | 0.024 | 0.067 | 0.027 | 0.061 | 0.021 |
| params refined | 218 | 820 | 496 | 415 | 343 | 424 |
| R1 | 0.035 | 0.035 | 0.028 | 0.027 | 0.027 | 0.025 |
| wR2 | 0.092 | 0.097 | 0.060 | 0.067 | 0.059 | 0.069 |
| $S$ | 0.991 | 1.023 | 0.988 | 1.040 | 1.014 | 1.057 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | −2.53 | −1.82 | −2.32 | −1.58 | −2.26 | −1.58 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 2.09 | 5.61 | 0.86 | 0.53 | 0.62 | 1.18 |

unity. The proton bound to the 2,2′-bipy molecule is disordered over the two nitrogen atoms, each position being involved in a hydrogen bond with one position of O9, and being given the relevant occupancy factor.

**Compound 5.** The hydrogen atoms bound to the nitrogen atoms of the 2,2′-bipy molecules, which are hydrogen bonded to one another, are likely disordered, and they have been arbitrarily introduced at the N1 and N3 positions.

**Compound 6.** The sulfonate group containing S2 is disordered over two positions with occupancy parameters first refined, then fixed to 0.7 and 0.3. The aromatic ring bonded to this group is necessarily disordered, as shown by some strongly anisotropic displacement parameters, but the two positions differ too slightly and could not be separated. Only one position of the sulfonate group is bound to U4 through O16a, the other position corresponding to the coordination of a water molecule (O16b).

Table 2. Environment of the Uranium Atoms in Compounds 1–6: Selected Bond Lengths (Å) and Angles (deg)[a]

| | | | | |
|---|---|---|---|---|
| **1** | U–O1 | 1.764(2) | O1–U–O2 | 178.19(11) |
| | U–O2 | 1.771(2) | O3–U–O4$^{i}$ | 75.68(8) |
| | U–O3 | 2.339(2) | O4$^{i}$–U–O6$^{j}$ | 73.76(8) |
| | U–O4$^{i}$ | 2.347(2) | O6$^{j}$–U–O8 | 71.70(8) |
| | U–O5 | 2.415(2) | O8–U–O5 | 67.56(7) |
| | U–O6$^{j}$ | 2.413(2) | O5–U–O3 | 71.55(9) |
| | U–O8 | 2.452(2) | | |
| **2** | U–O1 | 1.757(2) | O1–U–O2 | 177.61(15) |
| | U–O2 | 1.761(2) | O3–U–O4$^{i}$ | 74.05(10) |
| | U–O3 | 2.358(3) | O4$^{i}$–U–O6$^{j}$ | 74.72(10) |
| | U–O4$^{i}$ | 2.358(3) | O6$^{j}$–U–O8 | 71.48(10) |
| | U–O5 | 2.430(3) | O8–U–O5 | 70.18(9) |
| | U–O6$^{j}$ | 2.425(2) | O5–U–O3 | 69.72(10) |
| | U–O8 | 2.379(3) | | |
| **3** | U–O1 | 1.774(2) | O1–U–O1$^{i}$ | 179.07(13) |
| | U–O2 | 2.356(2) | O2–U–O4 | 73.61(7) |
| | U–O4 | 2.364(2) | O4–U–O4$^{i}$ | 73.75(10) |
| | U–O7 | 2.455(3) | O2–U–O7 | 69.52(5) |
| **4** | U–O1 | 1.773(4) | O1–U–O2 | 176.66(16) |
| | U–O2 | 1.768(4) | O3–U–O5 | 70.89(12) |
| | U–O3 | 2.419(4) | O5–U–O8 | 74.84(12) |
| | U–O4$^{i}$ | 2.407(4) | O8–U–O10 | 73.86(13) |
| | U–O5 | 2.386(4) | O10–U–O4$^{i}$ | 69.54(12) |
| | U–O8 | 2.336(4) | O4$^{i}$–U–O3 | 70.92(12) |
| | U–O10 | 2.382(4) | | |
| **5** | U1–O1 | 1.708(10) | O1–U1–O2 | 179.2(4) |
| | U1–O2 | 1.716(10) | O5–U1–O7 | 71.2(3) |
| | U1–O5 | 2.336(8) | O7–U1–O12 | 69.3(3) |
| | U1–O7 | 2.396(9) | O12–U1–O10 | 70.0(3) |
| | U1–O10 | 2.416(8) | O10–U1–O15 | 68.9(3) |
| | U1–O12 | 2.380(9) | O15–U1–O5 | 80.8(3) |
| | U1–O15 | 2.403(10) | | |
| | U2–O3 | 1.738(10) | O3–U2–O4 | 177.0(4) |
| | U2–O4 | 1.727(10) | O6–U2–O11$^{i}$ | 77.7(3) |
| | U2–O6 | 2.318(9) | O11$^{i}$–U2–O20 | 68.6(3) |
| | U2–O11$^{i}$ | 2.358(9) | O20–U2–O17 | 68.4(3) |
| | U2–O16 | 2.348(9) | O17–U2–O16 | 71.3(3) |
| | U2–O17 | 2.388(9) | O16–U2–O6 | 74.0(3) |
| | U2–O20 | 2.448(9) | | |
| **6** | U1–O1 | 1.749(4) | O1–U1–O2 | 178.34(17) |
| | U1–O2 | 1.757(4) | O9–U1–O11 | 71.19(13) |
| | U1–O9 | 2.341(4) | O11–U1–O16a | 74.29(16) |
| | U1–O11 | 2.426(3) | O16a–U1–O14 | 71.00(16) |
| | U1–O14 | 2.426(3) | O14–U1–O19 | 72.30(12) |
| | U1–O16a | 2.381(5) | O19–U1–O9 | 72.83(13) |
| | U1–O19 | 2.391(4) | | |
| | U2–O3 | 1.761(4) | O3–U2–O4 | 179.5(2) |
| | U2–O4 | 1.760(4) | O10–U2–O20 | 74.10(13) |
| | U2–O10 | 2.373(4) | O20–U2–O21 | 71.84(13) |
| | U2–O20 | 2.352(3) | O21–U2–O39 | 70.29(13) |
| | U2–O21 | 2.357(4) | O39–U2–O24 | 72.73(12) |
| | U2–O24 | 2.404(3) | O24–U2–O10 | 71.39(13) |
| | U2–O39 | 2.418(4) | | |
| | U3–O5 | 1.756(4) | O5–U3–O6 | 178.37(18) |
| | U3–O6 | 1.769(4) | O25–U3–O26 | 71.60(13) |
| | U3–O25 | 2.457(3) | O26–U3–O31 | 70.26(13) |
| | U3–O26 | 2.405(4) | O31–U3–O29 | 73.69(13) |
| | U3–O29 | 2.335(4) | O29–U3–O34 | 74.81(13) |
| | U3–O31 | 2.377(4) | O34–U3–O25 | 71.36(13) |
| | U3–O34 | 2.379(4) | | |
| | U4–O7 | 1.755(4) | O7–U4–O8 | 179.46(17) |
| | U4–O8 | 1.755(4) | O15$^{i}$–U4–O30 | 73.01(13) |
| | U4–O15$^{i}$ | 2.433(3) | O30–U4–O35 | 76.21(13) |
| | U4–O30 | 2.399(4) | O35–U4–O36 | 71.69(13) |
| | U4–O35 | 2.341(3) | O36–U4–O40 | 68.32(14) |
| | U4–O36 | 2.403(4) | O40–U4–O15$^{i}$ | 71.11(14) |
| | U4–O40 | 2.423(5) | | |

[a] Symmetry codes. **1**: i = 1 − *x*, −*y*, −*z*; j = *x*, −*y*, *z* + 1/2. **2**: i = 2 − *x*, 1 − *y*, 1 − *z*; j = *x*, 1/2 − *y*, *z* + 1/2. **3**: i = −*x*, *y*, 1/2 − *z*. **4**: i = 1 − *x*, 1 − *y*, 1 − *z*. **5**: i = *x* − 1, *y*, *z*. **6**: i = *x*, *y*, *z* + 1.

Crystal data and structure refinement parameters are given in Table 1 and selected bond lengths and angles in Tables 2–4. The molecular plots were drawn with ORTEP-3[18] and the views of the packings with VESTA.[19] The topological analyses were done with TOPOS,[20] and the search for π-stacking interactions was done with PLATON.[21]

## ■ RESULTS AND DISCUSSION

A general trend in all the present complexes is the metal chelation by the dianionic SB ligand (generated in situ from the anhydride), involving one oxygen atom from the sulfonate and one from the carboxylate to form a seven-membered ring (this coordination mode will be denoted *SC*-chelation in the following to differentiate it from chelation by a single functional group). This was also observed in the three uranyl complexes with SB and cucurbit[6]uril previously described,[10b] and the structures reported in the CSD show that it is a very common coordination mode with d-block and lanthanide ions too. The absence of such a chelate effect is likely a reason why attempts with 3- and 4-sulfobenzoic acids failed to give any solid state complex under similar conditions. While this chelate motif is ubiquitous in the present series, there is nevertheless much structural variability arising from the additional coordination of other oxygen atoms from SB, which often behaves as both a chelating and bridging ligand. The complexes involving only SB and water ligands will be described first, and they will be followed by those comprising also oxo or hydroxo bridges as a result of uranyl hydrolysis, and the uranyl–d-block metal heterometallic species.

**Uranyl Complexes Involving SB and Aquo Ligands.** These complexes were obtained in the presence of different amines, and all six of them display different structures. The complexes $[UO_2(SB)(H_2O)]$ (**1**) and $[UO_2(SB)(H_2O)]_2{\cdot}pyz$ (**2**) are the simplest since they involve no counterion (and **1** has no solvent molecule either). In both cases, besides *SC*-chelation, both the carboxylate and sulfonate groups are bridging bidentate (Figures 1 and 2). The average U–O(carboxylate) and U–O(sulfonate) bond lengths of 2.351(8) and 2.421(7) Å, respectively (including both compounds), do not differ significantly from the corresponding average values of 2.42(7) and 2.38(3) Å from the CSD. The uranium atom is in a pentagonal bipyramidal environment, as in most of the complexes reported herein, the coordination sphere being completed by a water molecule. The aromatic ring of SB is nearly perpendicular to the uranyl mean equatorial plane, with dihedral angles of 80.01(8)° in **1** and 89.03(9)° in **2**. The bridging carboxylate ensures the formation of centrosymmetric dimers with a central eight-membered ring, but the different connection of these dimers through sulfonate coordination

Table 3. Environment of the Uranium Atoms in Compounds 7 and 8: Selected Bond Lengths (Å) and Angles (deg)$^{a}$

| | | | | |
|---|---|---|---|---|
| **7** | U1–O1 | 1.780(4) | O1–U1–O1$^{i}$ | 180 |
| | U1–O4 | 2.608(5) | O4–U1–O5 | 48.33(12) |
| | U1–O5 | 2.660(4) | O5–U1–O9$^{i}$ | 65.88(14) |
| | U1–O9 | 2.216(4) | O9–U1–O4 | 65.80(13) |
| | U2–O2 | 1.784(4) | O2–U2–O3 | 173.6(2) |
| | U2–O3 | 1.783(4) | O4–U2–O6 | 70.71(14) |
| | U2–O4 | 2.537(4) | O6–U2–O5$^{j}$ | 82.85(14) |
| | U2–O5$^{j}$ | 2.486(4) | O5$^{j}$–U2–O9$^{k}$ | 68.65(14) |
| | U2–O6 | 2.410(4) | O9$^{k}$–U2–O9 | 71.30(16) |
| | U2–O9 | 2.247(4) | O9–U2–O4 | 66.69(13) |
| | U2–O9$^{k}$ | 2.250(4) | | |
| **8** | U1–O1 | 1.781(4) | O1–U1–O2 | 179.17(19) |
| | U1–O2 | 1.777(5) | O11–U1–O15 | 64.89(13) |
| | U1–O11 | 2.273(4) | O15–U1–O16 | 49.41(12) |
| | U1–O12 | 2.256(4) | O16–U1–O12 | 65.33(13) |
| | U1–O15 | 2.580(4) | O12–U1–O21 | 65.48(13) |
| | U1–O16 | 2.588(4) | O21–U1–O20 | 49.51(12) |
| | U1–O20 | 2.592(4) | O20–U1–O11 | 65.68(13) |
| | U1–O21 | 2.569(4) | | |
| | U2–O3 | 1.782(4) | O3–U2–O4 | 176.82(18) |
| | U2–O4 | 1.787(4) | O11–U2–O13 | 71.23(14) |
| | U2–O11 | 2.226(4) | O13–U2–O31$^{i}$ | 78.36(14) |
| | U2–O13 | 2.352(4) | O31$^{i}$–U2–O17 | 73.51(14) |
| | U2–O15 | 2.479(4) | O17–U2–O15 | 69.96(13) |
| | U2–O17 | 2.450(4) | O15–U2–O11 | 67.32(13) |
| | U2–O31$^{i}$ | 2.358(4) | | |
| | U3–O5 | 1.774(4) | O5–U3–O6 | 177.38(19) |
| | U3–O6 | 1.787(5) | O11–U3–O13 | 70.48(13) |
| | U3–O11 | 2.256(4) | O13–U3–O25 | 76.56(15) |
| | U3–O13 | 2.364(4) | O25–U3–O27 | 72.77(15) |
| | U3–O20 | 2.471(4) | O27–U3–O20 | 72.35(14) |
| | U3–O25 | 2.372(4) | O20–U3–O11 | 68.09(13) |
| | U3–O27 | 2.410(4) | | |
| | U4–O7 | 1.787(4) | O7–U4–O8 | 176.29(18) |
| | U4–O8 | 1.786(4) | O12–U4–O14 | 70.78(14) |
| | U4–O12 | 2.245(4) | O14–U4–O26$^{j}$ | 79.02(14) |
| | U4–O14 | 2.322(4) | O26$^{j}$–U4–O22 | 72.98(13) |
| | U4–O21 | 2.495(4) | O22–U4–O21 | 70.61(13) |
| | U4–O22 | 2.439(4) | O21–U4–O12 | 66.95(13) |
| | U4–O26$^{j}$ | 2.375(4) | | |
| | U5–O9 | 1.783(4) | O9–U5–O10 | 177.58(19) |
| | U5–O10 | 1.780(4) | O12–U5–O14 | 70.49(13) |
| | U5–O12 | 2.249(4) | O14–U5–O30 | 75.31(15) |
| | U5–O14 | 2.334(4) | O30–U5–O32 | 73.62(15) |
| | U5–O16 | 2.468(4) | O32–U5–O16 | 73.09(13) |
| | U5–O30 | 2.367(4) | O16–U5–O12 | 67.57(13) |
| | U5–O32 | 2.420(4) | | |

$^{a}$Symmetry codes. **7**: i = −*x*, −*y*, −*z*; j = *x* + 1, *y*, *z*; k = 1 − *x*, −*y*, −*z*. **8**: i = *x* − 1, *y*, *z*; j = *x* + 1, *y*, *z*.

Table 4. Environment of the Metal Atoms in Compounds 9–12: Selected Bond Lengths (Å) and Angles (deg)$^{a}$

| | | | | |
|---|---|---|---|---|
| **9** | U–O1 | 1.7670(19) | O1–U–O2 | 179.06(7) |
| | U–O2 | 1.7658(18) | O3–U–O5 | 71.05(6) |
| | U–O3 | 2.4144(16) | O5–U–O10 | 76.06(6) |
| | U–O4$^{i}$ | 2.3953(19) | O10–U–O8 | 72.69(6) |
| | U–O5 | 2.3585(18) | O8–U–O4$^{i}$ | 71.56(6) |
| | U–O8 | 2.4361(17) | O4$^{i}$–U–O3 | 69.17(6) |
| | U–O10 | 2.3705(18) | | |
| | Cu–O9 | 2.0544(17) | | |
| | Cu–N1 | 1.974(2) | | |
| | Cu–N2 | 2.015(2) | | |
| | Cu–N3 | 2.006(2) | | |
| | Cu–N4 | 2.139(2) | | |
| **10** | U–O1 | 1.759(2) | O1–U–O2 | 177.74(10) |
| | U–O2 | 1.768(2) | O3–U–O5 | 71.08(7) |
| | U–O3 | 2.334(2) | O5–U–O8 | 71.33(7) |
| | U–O4$^{i}$ | 2.357(2) | O8–U–O10 | 73.48(7) |
| | U–O5 | 2.424(2) | O10–U–O4$^{i}$ | 68.20(7) |
| | U–O8 | 2.302(2) | O4$^{i}$–U–O3 | 76.90(7) |
| | U–O10 | 2.4640(19) | | |
| | Cu–O13 | 1.955(2) | | |
| | Cu–O14 | 1.990(2) | | |
| | Cu–O15 | 2.167(2) | | |
| | Cu–N1 | 2.050(2) | | |
| | Cu–N2$^{j}$ | 2.042(2) | | |
| **11** | U–O1 | 1.765(2) | O1–U–O2 | 178.17(10) |
| | U–O2 | 1.767(2) | O3–U–O5 | 72.72(7) |
| | U–O3 | 2.3689(19) | O5–U–O8 | 69.47(7) |
| | U–O5 | 2.363(2) | O8–U–O10 | 73.91(7) |
| | U–O8 | 2.382(2) | O10–U–O13 | 73.89(7) |
| | U–O10 | 2.3860(19) | O13–U–O3 | 70.80(7) |
| | U–O13 | 2.475(2) | | |
| | Cu–O4 | 1.9300(19) | | |
| | Cu–O9$^{j}$ | 2.0130(18) | | |
| | Cu–O14 | 2.141(3) | | |
| | Cu–N1 | 2.024(2) | | |
| | Cu–N2$^{i}$ | 2.049(2) | | |
| **12** | U–O1 | 1.7773(17) | O1–U–O2 | 179.14(7) |
| | U–O2 | 1.7662(18) | O3–U–O5 | 72.46(6) |
| | U–O3 | 2.3408(16) | O5–U–O13 | 71.94(6) |
| | U–O5 | 2.4212(18) | O13–U–O10 | 68.81(7) |
| | U–O8 | 2.3372(19) | O10–U–O8 | 71.92(7) |
| | U–O10 | 2.3822(18) | O8–U–O3 | 75.84(7) |
| | U–O13 | 2.4331(18) | | |
| | Ni–O4 | 1.9957(18) | | |
| | Ni–O14 | 2.0553(19) | | |
| | Ni–N1 | 2.082(2) | | |
| | Ni–N2$^{i}$ | 2.125(2) | | |
| | Ni–N3 | 2.095(2) | | |
| | Ni–N4$^{j}$ | 2.103(2) | | |

$^{a}$Symmetry codes. **9**: i = −*x*, −*y*, 1 − *z*. **10**: i = 1 − *x*, 1 − *y*, −*z*; j = *x* − 1, *y*, *z*. **11**: i = 2 − *x*, 2 − *y*, 1 − *z*; j = *x* + 1, *y*, *z*. **12**: i = 1 − *x*, 1 − *y*, −*z*; j = 1 − *x*, *y*, −*z* − 1/2.

results in different overall architectures. In **1**, these dimers are associated one to the other along the *c* axis by double sulfonate bridges, resulting in the formation of a one-dimensional polymer with the total point symbol ($4^2$, 6). These chains comprise a central ribbon of uranyl polyhedra surrounded on its two sides by the aromatic rings, and they are stacked along the *b* axis to form sheets of interdigitated chains. There may be an intrachain π-stacking interaction [centroid···centroid distance 4.113(2) Å], but no significant interchain one [shortest centroid···centroid distance 5.042(2) Å]. Neighboring sheets along the *a* axis are connected to one another by the hydrogen bonds involving the water ligand (with the oxo atom O2 and the sulfonate O7 as acceptors). In **2**, each dimer is connected to four others by one sulfonate bridge each, and a two-dimensional assembly parallel to the *bc* plane is formed, with the total point symbol (4, $8^2$). Simplified representations of the two networks are shown in Scheme 1. The sheets in **2** are

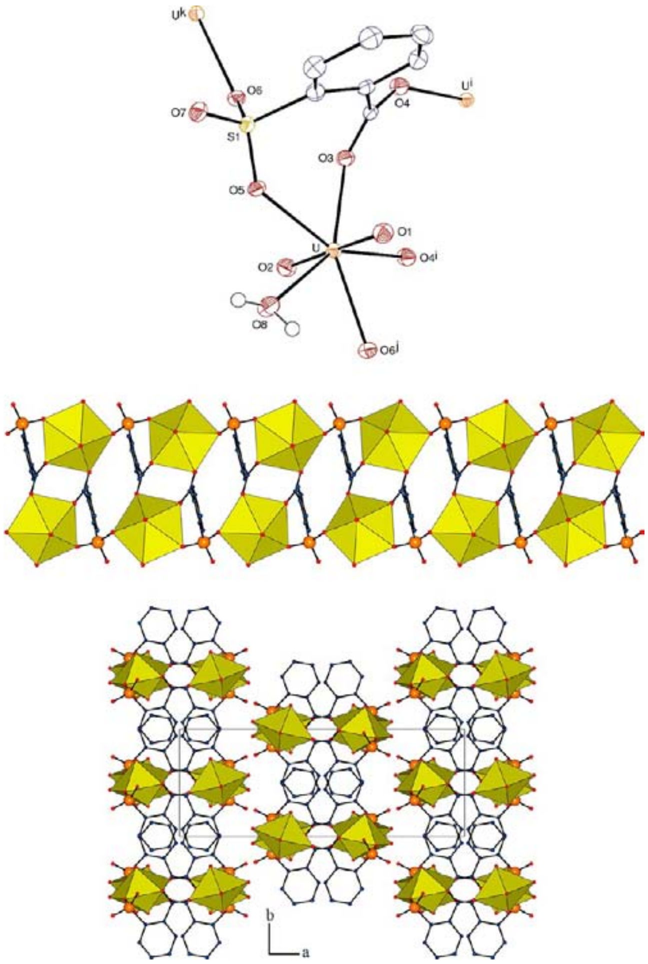


**Figure 1.** Top: View of complex **1**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted. Symmetry codes: i = 1 − *x*, −*y*, −*z*; j = *x*, −*y*, *z* + 1/2; k = *x*, −*y*, *z* − 1/2. Middle: View of the one-dimensional assembly. Bottom: Packing with the chains viewed end-on, showing the uranium coordination polyhedra and with hydrogen atoms omitted.

stacked along the *a* axis in such a way that some interdigitation is present, but there is no significant π-stacking interaction. While the base used for the synthesis of **1**, 2-aminopyridine ($pK_a$ = 6.86), is absent from the final product, which is a unique occurrence in this series of compounds, the much less basic pyrazine ($pK_{a1}$ = 0.37) is present in its unprotonated form in **2**. The structural differences observed may thus result from the structure-directing effect of the latter. The centrosymmetric pyrazine molecules occupy interlayer spaces and contribute to the cohesion of the whole by being hydrogen bonded to water ligands from the two neighboring sheets [O8···N1 2.704(4) Å, O8−H···N1 178°]; all other hydrogen bonds are intralayer ones.

Three complexes were obtained with bipyridine molecules as bases, $[2,2'\text{-bipyH}]_2[UO_2(SB)_2(H_2O)]\cdot 4H_2O$ (**3**), $[4,4'\text{-bipyH}_2]_2[UO_2(SB)_2]_2$ (**4**), and $[4,4'\text{-bipyH}]_2[(UO_2)_2(SB)_3(H_2O)]\cdot 4H_2O$ (**5**). In all cases, the bipy molecules ($pK_{a1}$ of 4.34 and 4.82 for 2,2′- and 4,4′-bipy, respectively) are either mono- or diprotonated and act as counterions. Complex **3** is a molecular species with the uranyl ion bound in its equatorial plane to two *SC*-chelating SB ligands and one water ligand, with the uranium and water oxygen atoms being located on a binary axis of symmetry (Figure 3). The bond lengths and angles are unexceptional. The complex anions are located in sheets parallel to the *bc* plane, which are separated by the counterions. No direct hydrogen bond links the cations and anions, but they are connected through an intricate, and partially disordered, hydrogen bond network involving solvent water molecules. π-Stacking interactions are formed between SB and 2,2′-bipyH [centroid···centroid distance 3.873(3) Å, dihedral angle 6.3(3)°] and also between neighboring 2,2′-bipyH cations [centroid···centroid distance 3.852(3) Å, dihedral angle 3.7(3)°].

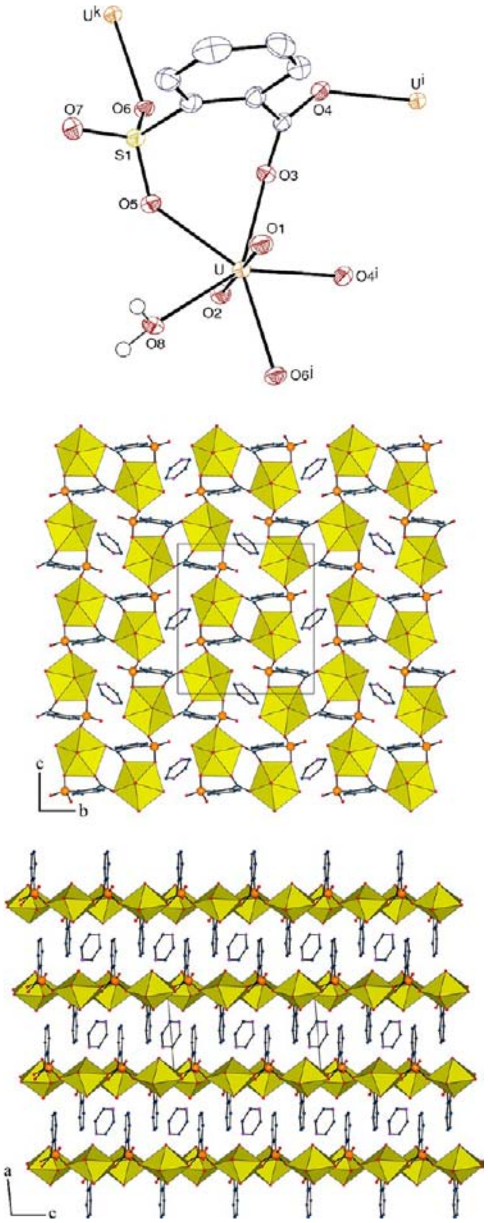
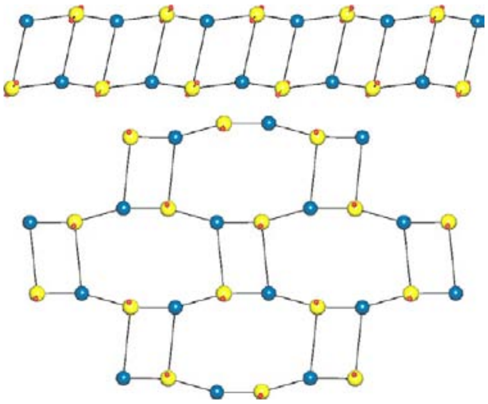


**Figure 2.** Top: View of complex **2**. Displacement ellipsoids are drawn at the 50% probability level. The pyz molecule and carbon-bound hydrogen atoms are omitted. Symmetry codes: i = 2 − *x*, 1 − *y*, 1 − *z*; j = *x*, 1/2 − *y*, *z* + 1/2; k = *x*, 1/2 − *y*, *z* − 1/2. Middle: View of the two-dimensional assembly. Bottom: Packing with the layers viewed edge-on, showing the uranium coordination polyhedra and with hydrogen atoms omitted.

Complex **4** is also molecular, but it is a centrosymmetric, carboxylate-bridged dimer (Figure 4). The central part is analogous to that in the dimers found as subunits in **1** and **2**, but the atom O6^j and the water molecule in the latter are

**Scheme 1. Simplified Views of the Assemblies in 1 (Top) and 2 (Bottom)**[a]



[a]Uranium: yellow. Oxygen: red. SB centroid: blue (water molecules are excluded).

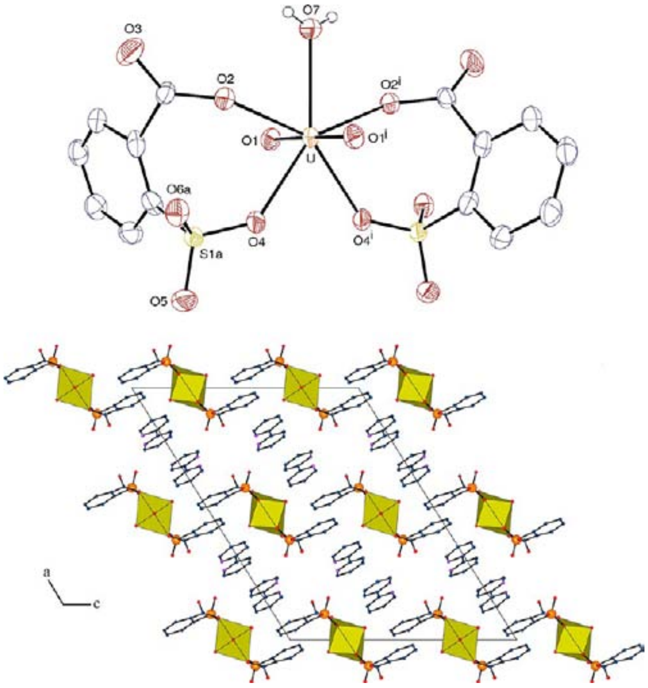


**Figure 3.** Top: View of complex **3**. Displacement ellipsoids are drawn at the 30% probability level. Counterions, solvent molecules, and carbon-bound hydrogen atoms are omitted. Only one position of the disordered parts is represented. Symmetry code: i = −*x*, *y*, 1/2 − *z*. Bottom: View of the packing with solvent molecules and hydrogen atoms omitted.

replaced here by another *SC*-chelating SB anion. The U−O bond length with the monodentate carboxylate [2.336(4) Å] is slightly shorter than the average with the bridging one [2.413(6) Å], while the average U−O(sulfonate) bond length of 2.384(2) Å is unexceptional. Both SB aromatic rings are nearly perpendicular to the uranyl equatorial plane, with dihedral angles of 81.05(13) and 79.50(13)°. Neighboring dimers are connected to one another along the [1 0 1] axis by two doubly hydrogen bonded 4,4′-bipy$H_2$ molecules [N1···O3 2.801(6) Å, N1−H···O3 165°; N2···O9$^i$ 2.685(6) Å, N2−H···O9$^i$ 171°, i = *x* + 1, *y*, *z* + 1], thus giving hydrogen bonded one-dimensional polymers along this direction. These chains are tightly packed with one another to give sheets parallel to the *ac* plane, with sheets related to one another by the glide plane alternating along the *b* axis.

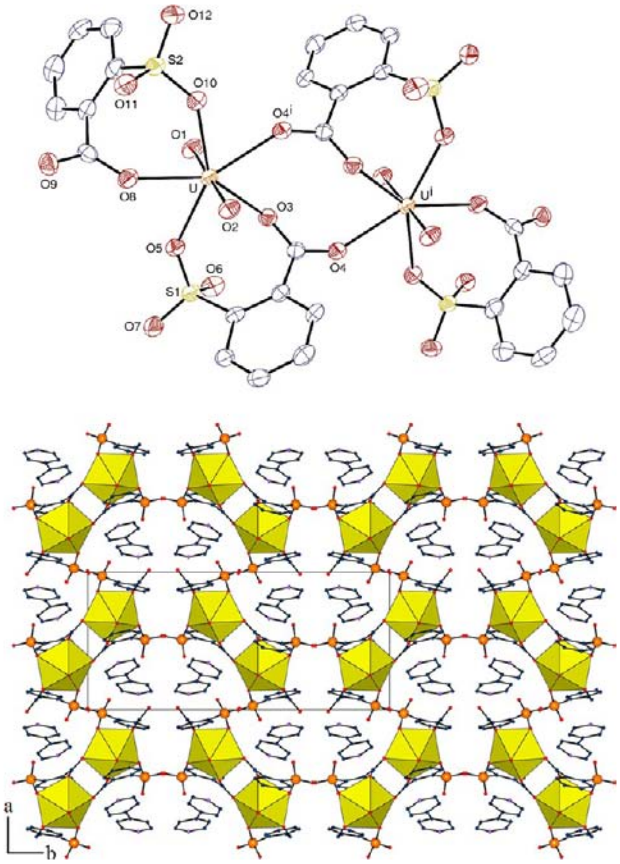


**Figure 4.** Top: View of complex **4**. Displacement ellipsoids are drawn at the 50% probability level. Counterions and hydrogen atoms are omitted. Symmetry code: i = 1 − *x*, 1 − *y*, 1 − *z*. Bottom: View of the packing with hydrogen atoms omitted.

4,4′-Bipy is monoprotonated only in complex **5**, which was obtained under conditions different from those leading to **4**, the concentration of the reactants being larger and the solution having been left to evaporate without being first heated for a long period (**5** is the only compound in this series to have been obtained under non-hydrothermal conditions). Crystals of **5** were mixed with large, colorless crystals of (4,4′-bipy$H_2$)-$(NO_3)_2$.[22] Two crystallographically independent uranium ions are present, which possess different coordination environments (Figure 5). U1 is bound to two *SC*-chelating SB ligands, with the two sulfonate groups side-by-side in the coordination sphere, while the sulfonate of one ligand is adjacent to the carboxylate of the other in complex **4**. The last coordination site around U1 is occupied by a carboxylate oxygen atom from a third SB anion, which is chelating atom U2. The coordination sphere of U2 is completed by the carboxylate atoms O6 and O11$^i$ and one water molecule. A carboxylate-bridged dimeric assembly analogous to those in the previous compounds is thus formed, with the environment of U1 close to that found in **4**, while the environment of U2 is similar to that in **1** and **2**. These dimeric subunits are assembled into a one-dimensional assembly running along the *a* axis. The chains are arranged in sheets parallel to *ac*, with all the aromatic rings located on the same side, and adjoining sheets related by the inversion center are themselves associated into double layers with the aromatic rings located in the inside space (with however no significant

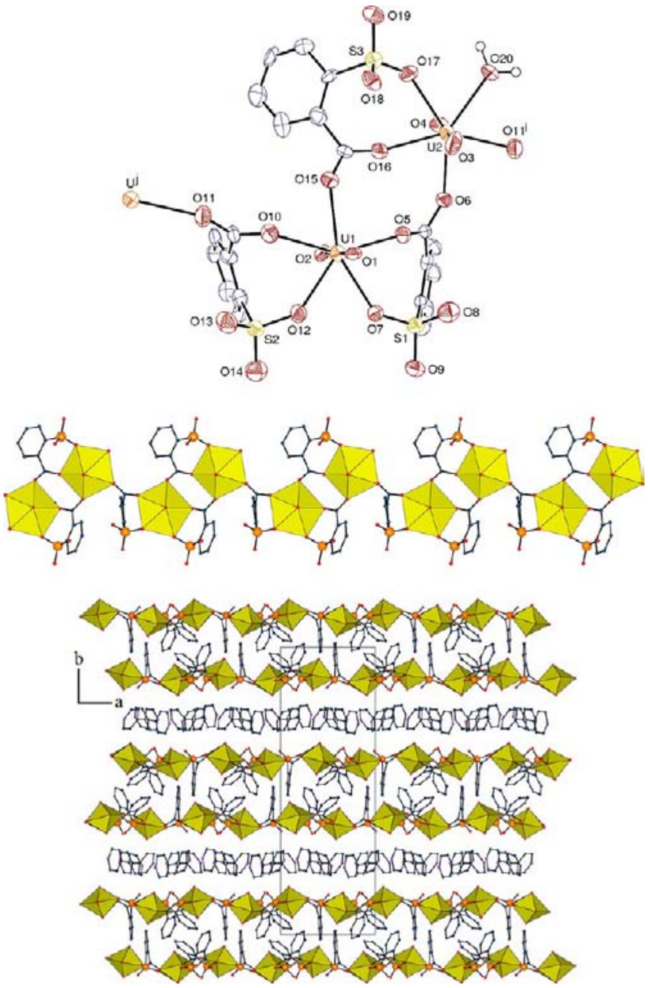


**Figure 5.** Top: View of complex **5**. Displacement ellipsoids are drawn at the 50% probability level. Counterions, solvent molecules, and carbon-bound hydrogen atoms are omitted. Symmetry codes: i = $x - 1$, $y$, $z$; j = $x + 1$, $y$, $z$. Middle: View of the one-dimensional assembly. Bottom: Packing with solvent molecules and hydrogen atoms omitted.

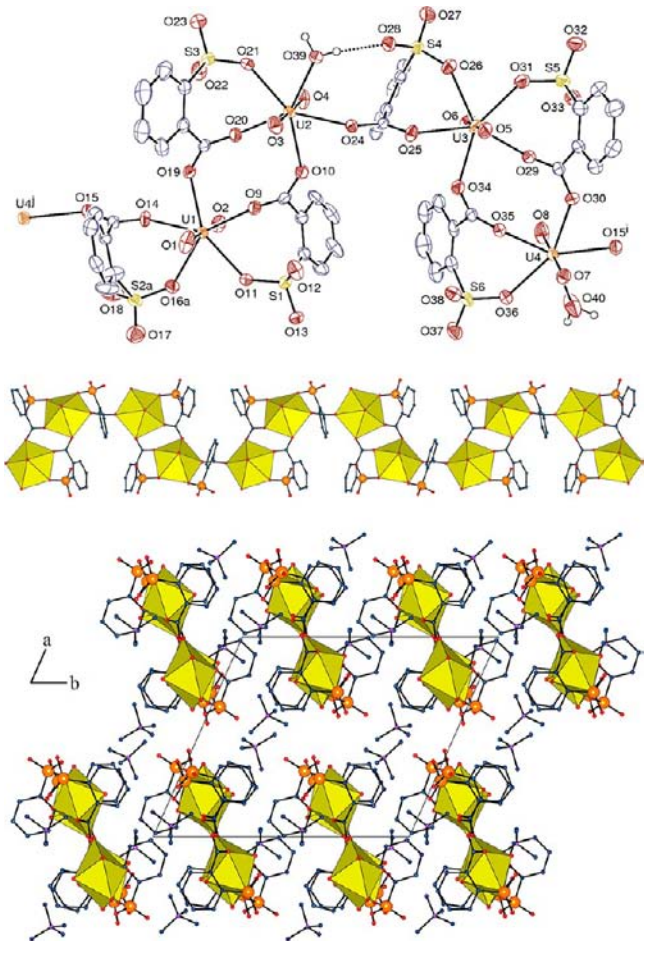


**Figure 6.** Top: View of complex **6**. Displacement ellipsoids are drawn at the 40% probability level. Counterions, solvent molecules, and carbon-bound hydrogen atoms are omitted. Only one position of the disordered part is represented. The hydrogen bond is shown as a dashed line. Symmetry codes: i = $x$, $y$, $z + 1$; j = $x$, $y$, $z - 1$. Middle: View of the one-dimensional assembly. Bottom: View of the packing with solvent molecules and hydrogen atoms omitted.

$\pi$-stacking interactions). The water ligands are involved in hydrogen bonds with solvent water molecules. The bilayers are separated from one another along the *b* axis by sheets of 4,4′-bipyH cations, which are hydrogen bonded to one another [N···N distances 2.718(14) and 2.758(16) Å, N−H···N angles 178 and 177°].

Two complexes were obtained with tetramethylammonium hydroxide as a base, one of them, $[NMe_4]_2[(UO_2)_2(SB)_3(H_2O)_{1.15}]\cdot 1.35H_2O$ (**6**), with only water as an additional ligand while the other one contains also oxo ions and will be discussed within the next series. The asymmetric unit in **6** contains four uranyl ions (Figure 6) in environments which are closely related to those in **5** (if the disorder affecting one SB ligand is disregarded; see Experimental Section). Atoms U1 and U3 are *SC*-chelated by two SB ligands, as U1 in **5**, and U2 and U4 are bound to one chelating and two monodentate SB, and one water molecule, as U2 in **5**. Two dimers (U1/U2 and U3/U4) are thus created, but, instead of successive dimers in the chain being related to one another by translations as in **5**, the two dimers in the tetranuclear asymmetric unit in **6** are assembled into a motif of roughly half-circular geometry. The one-dimensional assembly, generated by translations of this tetranuclear subunit, is a zigzag chain parallel to the *c* axis. Another difference with **5** is that the aromatic rings are located on either side (in particular, the two chelating ligands are pointing in opposite directions around both U1 and U3). These chains are closely packed to form layers parallel to the *bc* plane (with no significant $\pi$-stacking interactions), which are separated by the tetramethylammonium counterions.

**Uranyl Complexes Involving SB and Oxo/Hydroxo Ligands.** The second complex obtained with $NMe_4OH$, $[NMe_4]_2[(UO_2)_3(SB)_2O_2]$ (**7**), was obtained under conditions identical to those yielding **6**, but for the presence of an equimolar amount of $Cu(NO_3)_2\cdot 2.5H_2O$, which was aimed at synthesizing a heterometallic complex. As an unexpected result of this difference, complex **7** contains additional $\mu_3$-oxo anions and displays structural features completely different from those of the previous compounds. The asymmetric unit contains two independent uranium atoms, one of them (U1) being located on an inversion center (Figure 7). U1 is chelated by the carboxylate group of the SB ligand (and its image by the inversion center) and is bound to two $\mu_3$-oxo anions, the uranium coordination environment being hexagonal bipyramidal, with an average U−O(carboxylate) bond length of 2.63(3) Å, which is at the upper end of the range calculated from the CSD for chelating carboxylates and six-coordinate equatorial

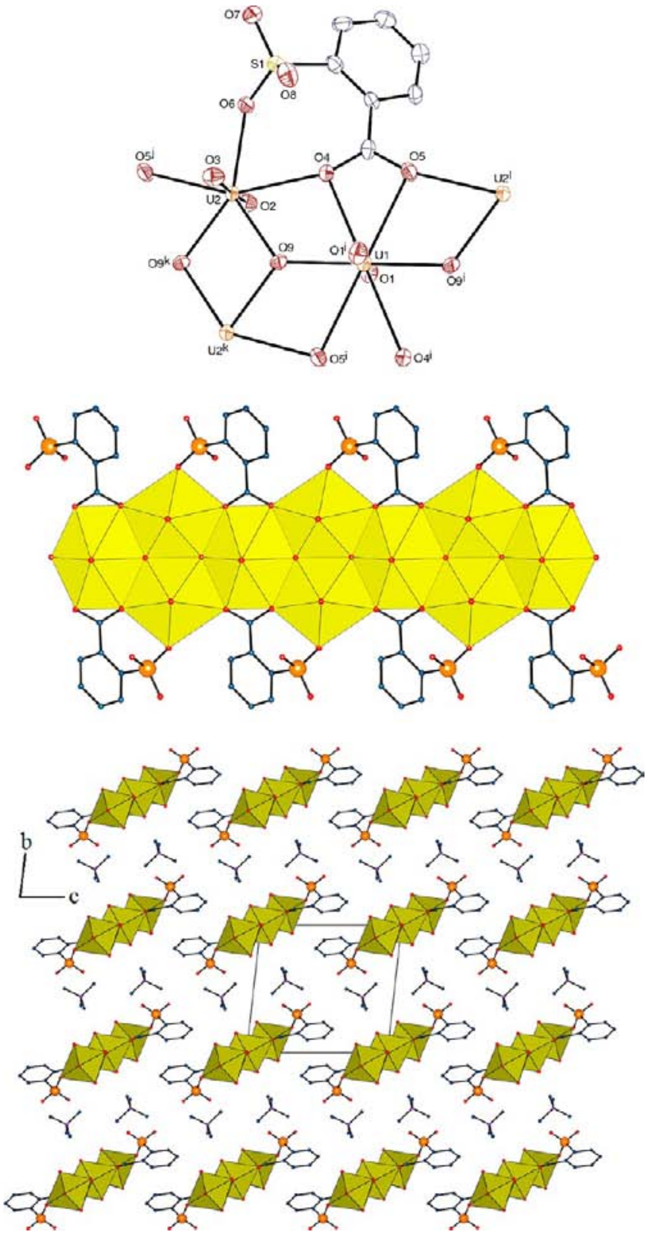


**Figure 7.** Top: View of complex **7**. Displacement ellipsoids are drawn at the 50% probability level. Counterions and hydrogen atoms are omitted. Symmetry codes: i = −*x*, −*y*, −*z*; j = *x* + 1, *y*, *z*; k = 1 − *x*, −*y*, −*z*; l = *x* − 1, *y*, *z*. Middle: View of the one-dimensional assembly. Bottom: View of the packing with chains viewed end-on and hydrogen atoms omitted.

environments [mean value 2.48(5) Å], which can be ascribed to both oxygen atoms being coordinated in $\mu_2$ mode. U2 is *SC*-chelated by the SB ligand, and its pentagonal bipyramidal environment is completed by two $\mu_3$-oxo anions and one carboxylate atom from a second SB ligand. The U2−O(carboxylate) average bond length of 2.51(3) Å is expectedly slightly larger than in the previous compounds. The average U−O($\mu_3$-oxo) bond length of 2.238(15) Å and the average U−O($\mu_3$-oxo)−U angle of 120(8)° (with the sum of the three angles amounting to 359.7°) are unexceptional [the average value from the CSD for similar bonds is 2.25(6) Å]. The polyhedron around U1 shares four edges with the polyhedra of the four proximal U2 atoms, while two U2 atoms share the edge containing the two bridging $\mu_3$-oxo anions. The resulting assembly is a one-dimensional planar ribbon of tightly packed $[(UO_2)_3O_2]^{2+}$ subunits running along the *a* axis, with SB ligands located at both edges. The $\mu_3$-oxo-centered trinuclear motif $[(UO_2)_3O]^{4+}$ is quite common in uranyl chemistry,[10a,23] as well as the tetranuclear $[(UO_2)_4O_2]^{4+}$ one,[23f,24] having been found in both discrete and polymeric species, with variations as to the coordination number of the metal atoms and the number of shared edges. One-dimensional polymers built around $\mu_3$-oxo or hydroxo bridges are also known,[10a,25] but the present secondary building unit (SBU), with an infinite $\mu_3$-oxo-bridged array of uranyl ions and a maximum number of shared edges (enabled by the coexistence of pentagonal and hexagonal bipyramidal polyhedra), is quite unusual among uranyl−organic polymers,[25b] whereas similar motifs are found in mineral species.[26] These planar ribbons are connected to one another along the *c* axis by parallel-displaced π-stacking interactions [centroid···centroid distance 3.567(4) Å, offset 1.28 Å] so as to form sheets parallel to the *ac* plane,

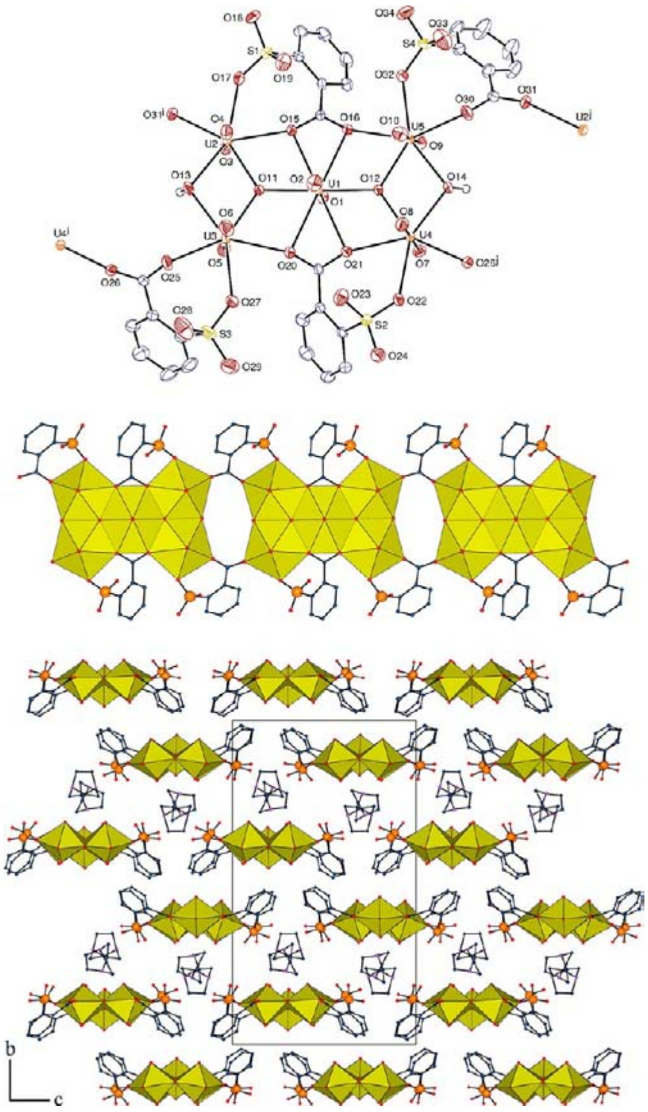


**Figure 8.** Top: View of complex **8**. Displacement ellipsoids are drawn at the 50% probability level. Counterions, solvent molecules, and carbon-bound hydrogen atoms are omitted. Symmetry codes: i = *x* − 1, *y*, *z*; j = *x* + 1, *y*, *z*. Middle: View of the one-dimensional assembly. Bottom: View of the packing with chains viewed end-on and solvent molecules and hydrogen atoms omitted.

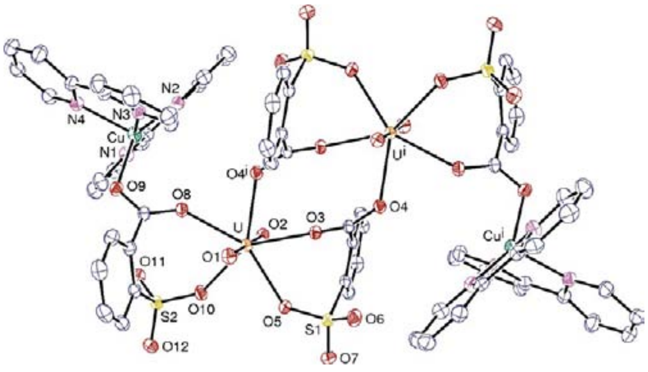


**Figure 9.** View of complex **9**. Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms are omitted. Symmetry code: i = −*x*, −*y*, 1 − *z*.

which are separated from one another by the $NMe_4^+$ counterions.

The complex formed in the presence of DABCO (p$K_{a1}$ = 8.82) comprises both oxo and hydroxo anions. The asymmetric unit in $[H_2DABCO]_2[(UO_2)_5(SB)_4O_2(OH)_2]\cdot 4H_2O$ (**8**) corresponds to one formula unit, the five uranyl ions being crystallographically independent (Figure 8). The geometry is very close to that in complex **7**, with atom U1 chelated by two carboxylate groups and bound to two $\mu_3$-oxo anions in trans positions, and atoms U2−U5 *SC*-chelated by one SB ligand each. However, the formation of an infinite $\mu_3$-oxo-bridged chain is disrupted here by the replacement of the second $\mu_3$-oxo anion bound to U2 in **7** by a $\mu_2$-hydroxo anion. The average U1−O(carboxylate) bond length is 2.582(9) Å, while the average for the other four uranium atoms is 2.42(6) Å, slightly shorter than in **7** since some carboxylate oxygen atoms are no longer $\mu_2$-coordinated. The average U−O($\mu_3$-oxo) and U−O($\mu_2$-hydroxo) bond lengths of 2.251(14) and 2.343(16) Å, respectively, are unexceptional [the average value from the CSD for the latter is 2.34(3) Å]. The SBU in **8** is thus pentanuclear and comprises a central uranium atom in hexagonal bipyramidal coordination surrounded by four pentagonal bipyramidal centers, with a total of six shared edges. Although higher nuclearity SBUs are known, such as hexa-[27] and octanuclear[20] ones, this seems to be the first instance of a pentanuclear one based on $\mu_3$-oxo bridges. However, it is notable that a pentanuclear motif of similar geometry, but with oxo and hydroxo anions replaced by fluoride anions, and with phosphate lateral ligands, has previously been described.[28] These pentanuclear units are flanked by four chelating SB ligands, and carboxylate groups doubly bridge neighboring SBUs along the *a* axis, thus giving a one-dimensional assembly. These chains are derived from those in **7**, with one uranium atom in hexagonal bipyramidal coordination out of every two being removed, and replacement of the corresponding $\mu_3$-oxo by $\mu_2$-hydroxo bridges. However, in contrast to **7**, all aromatic rings are on the same side of the uranyl ribbon. The chains are positioned side-by-side in planes parallel to *ac*. Two such planes related by an inversion center are facing each other through their aromatic rings, and they are held together by parallel-displaced $\pi$-stacking interactions involving only the aromatic rings bound to S1 and S4, located on the same ribbon edge [centroid···centroid distances 3.671(3) and 3.793(4) Å, offsets 1.32 and 1.54 Å]. The double layers thus formed are separated from one another by the $H_2DABCO^{2+}$ counterions. The hydroxy ions and one counterion are hydrogen bonded to water molecules, while the other counterion connects one bilayer to its image through the diagonal glide plane [N1···O13 2.873(9) Å, N1−H···O13 161°; N2···O29$^i$ 2.739(9) Å, N2−H···O29$^i$ 151°, i = *x* − 1/2, 1/2 − *y*, *z* − 1/2]. The lattice water molecules ensure further intra- and interlayer hydrogen bonding connections.

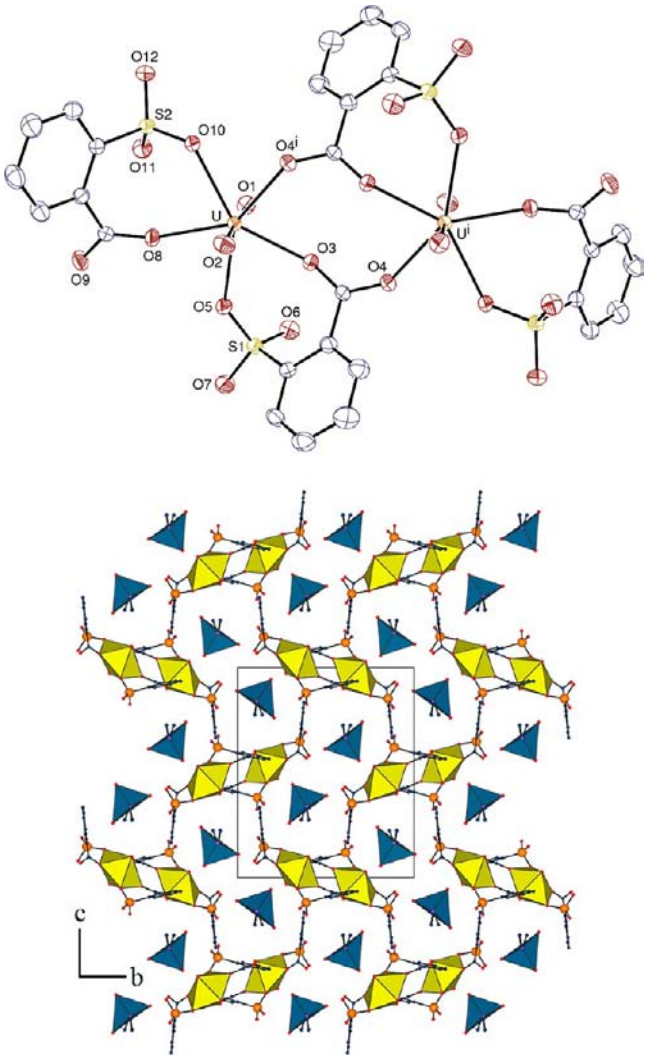


**Figure 10.** Top: View of complex **10**. Displacement ellipsoids are drawn at the 50% probability level. Counterions, solvent molecules, and hydrogen atoms are omitted. Symmetry code: i = 1 − *x*, 1 − *y*, −*z*. Bottom: View of the packing with solvent molecules and hydrogen atoms omitted. The uranyl coordination polyhedra are in yellow and those of copper in blue.

**Uranyl−3d-Block Metal Heterometallic Complexes.** The large potential denticity of SB and its having two different functionalities make it a suitable ligand for the synthesis of heterometallic complexes. No uranyl−lanthanide species could be isolated in this case, but four complexes involving both uranyl and 3d-block metal ions ($Cu^{2+}$, $Ni^{2+}$) and additional ligands with nitrogen donors (2,2′- and 4,4′-bipyridine, bipyrimidine) were obtained. The complex $[UO_2Cu(SB)_2(2,2'\text{-bipy})_2]_2\cdot 2H_2O$ (**9**) is a centrosymmetric, heterometallic tetranuclear species (Figure 9). The uranyl ion is *SC*-chelated by two SB ligands, with the sulfonate groups being adjacent, as in complexes **3**, **5**, and **6**, and dimerization is due to the bridging bidentate carboxylate groups, as in **4**, **5**, and **6**. In contrast to the two latter cases, the propagation of this dimeric motif is stopped by the

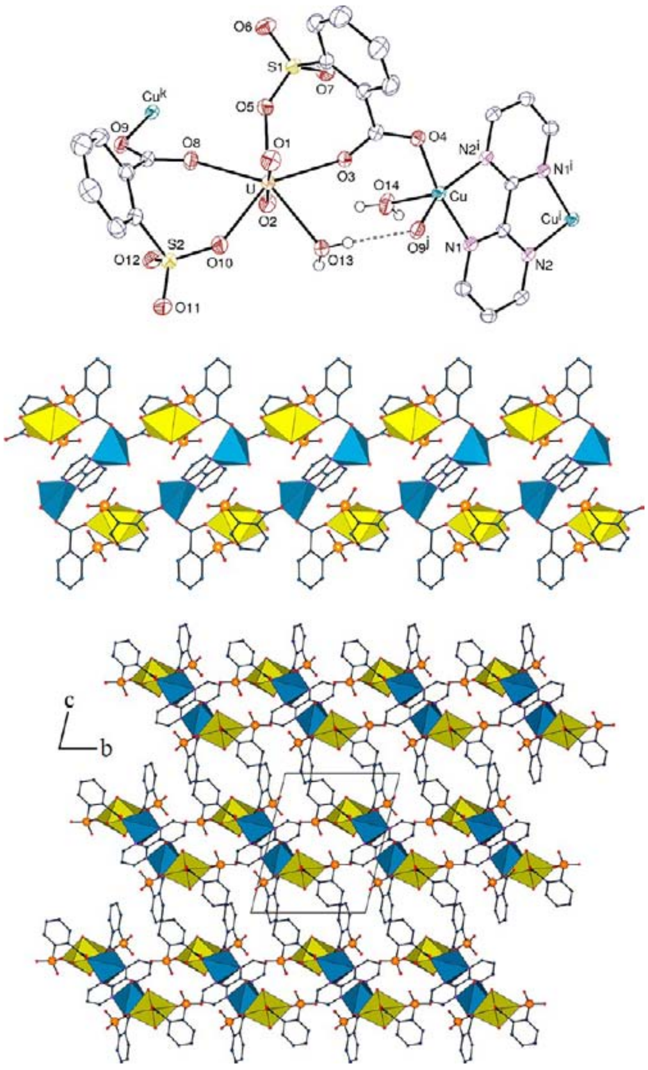


**Figure 11.** Top: View of complex **11**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted. The hydrogen bond is shown as a dashed line. Symmetry codes: i = 2 − *x*, 2 − *y*, 1 − *z*; j = *x* + 1, *y*, *z*; k = *x* − 1, *y*, *z*. Middle: View of the one-dimensional assembly. Bottom: View of the packing with hydrogen atoms omitted. The uranyl coordination polyhedra are in yellow and those of copper in blue.

lateral carboxylate groups being bound to copper atoms with two terminal 2,2′-bipy ligands. The U−O bond lengths are unexceptional, and the copper atom is in a distorted square pyramidal environment with atom N4 at the apex and bond lengths in the usual range.

The uranyl- and copper-containing parts are separated in the complex formed in the presence of 4,4′-bipy, $[Cu(4,4'\text{-bipy})(H_2O)_3]_2[UO_2(SB)_2]_2 \cdot 2H_2O$ (**10**). Uranyl cations form a centrosymmetric, dimeric complex identical to that previously encountered in complex **4** and which will not be described further (Figure 10). The copper atoms, in a square pyramidal environment with the two nitrogen atoms in trans positions and the water atom O15 at the apex, form a one-dimensional polymer parallel to the *a* axis. When viewed down this axis, the packing of uranyl dimers displays channels with an elongated section occupied by two $[Cu(4,4'\text{-bipy})(H_2O)_3]^{2+}$ chains related to one another by an inversion center.

More interesting results have been obtained with the bis-chelating ligand bipyrimidine associated with $Cu^{2+}$ or $Ni^{2+}$ cations. In both complexes $[(UO_2)_2Cu_2(SB)_4(\text{bipym})(H_2O)_4]$ (**11**) and $[UO_2Ni(SB)_2(\text{bipym})(H_2O)_2] \cdot 3H_2O$ (**12**), the single uranyl ion in the asymmetric unit is *SC*-chelated by two SB ligands (with the difference that the two carboxylate groups are adjacent in the coordination sphere in **12**, while one sulfonate is next to a carboxylate in **11**) and a water molecule completes the environment (Figures 11 and 12). In **11**, the copper atom is bound to two carboxylate groups from two different uranyl complex moieties, one chelating bipym, and one water molecule, in a distorted square pyramidal environment with the water atom O14 at the apex. Each SB ligand bridges uranium and copper atoms, thus generating a chain along the *a* axis in which the individual motifs are related to one another by translations, while the bipym ligand bridges two copper atoms and thus connects two chains related by an inversion center to give a ladderlike one-dimensional assembly of total point

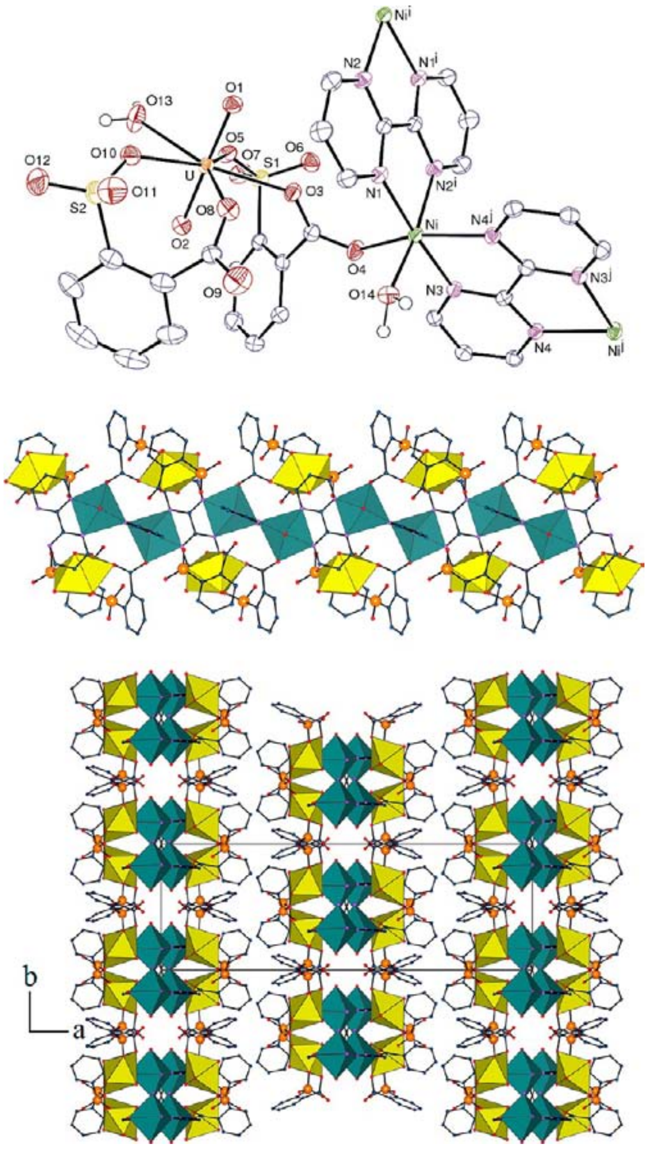
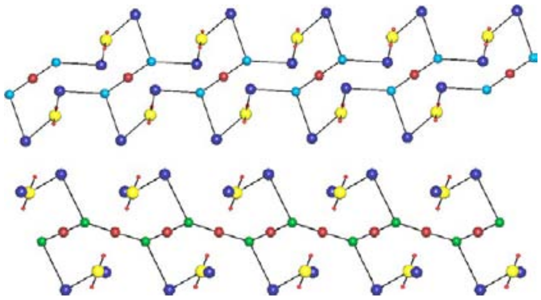


**Figure 12.** Top: View of complex **12**. Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules and carbon-bound hydrogen atoms are omitted. Symmetry codes: i = 1 − *x*, 1 − *y*, −*z*; j = 1 − *x*, *y*, −*z* − 1/2. Middle: View of the one-dimensional assembly. Bottom: View of the packing with solvent molecules and hydrogen atoms omitted. The uranyl coordination polyhedra are in yellow and those of nickel in green.

symbol $(12^2, 20)_2(12)_7$. In contrast, the nickel atom in **12** is bound to two bipym molecules, one carboxylate group, and one water molecule, giving a distorted octahedral environment. Only one of the SB ligands bridges uranium and nickel atoms, so that the $[UO_2(SB)_2(H_2O)]^{2-}$ moieties are merely decorating units located on the edges of the $[Ni(bipym)(H_2O)]^{2+}$ one-dimensional zigzag chain directed along the *c* axis. The difference between the two assemblies is represented in Scheme 2, and it appears to be due to one more bipym ligand being introduced in **12**, creating a direct link between 3d transition metals which replaces a SB bridge between these metals and uranyl ions. A search of the CSD shows that, whereas several Cu(bipym) one-dimensional polymers are known, **12** is the first example of such a chain with Ni atoms.

**Scheme 2. Simplified Views of the Assemblies in 11 (Top) and 12 (Bottom)**[a]



[a]Uranium: yellow. Copper: light blue. Nickel: green. Oxygen: red. SB centroid: dark blue. bipym centroid: dark red (water molecules are excluded).

## CONCLUSIONS

The structures of the complexes formed by 2-sulfobenzoate with uranyl ions in the presence of different organic bases were investigated. In all complexes, sulfonate complexation occurs, notwithstanding the use of hydrous synthesis conditions, generally considered to be unfavorable for such a weak donating group.[4] The dianionic SB ligand is always chelating one uranyl ion through one carboxylate oxygen atom and one sulfonate oxygen atom, a coordination mode which is most common with this molecule. The absence of crystallized uranyl complexes with 3- and 4-sulfobenzoates when similar conditions are used points to the importance of the chelate effect to promote sulfonate coordination and to provide a suitably stable building block. It has recently been shown that sulfonate groups present in humic acids played only a minor role in uranyl fixation, due to low complexation constants and also to the low sulfur content of these substances,[13] however the present results, as well as previous ones involving 4,5-dihydroxy-1,3-benzenedisulfonate,[10a,29] suggest that the presence of strongly coordinating oxygen donors at a suitable distance from the sulfonate for chelation to be possible deserves to be taken into account. What is quite remarkable with 2-sulfobenzoate is that, given this general chelating coordination trend, a large array of structures can nevertheless be obtained by changing the amines used as bases, which are present as neutral or protonated, cationic species in the final products, or even altogether absent. This is exemplified in the series of uranyl complexes formed with six amines, which comprises eight different architectures, either molecular, one-dimensional, or two-dimensional, thus demonstrating the extreme sensitivity of the $UO_2$−SB system to structure-directing effects. This structural variety is even increased, and rendered even more unpredictable, by the additional oxo and hydroxo anions resulting in some cases from hydrolysis. This gives rise to two unusual secondary building units: a $[(UO_2)_3O_2]_\infty$ linear polymer with an alternation of pentagonal and hexagonal bipyramidal centers sharing a maximum number of edges, and the unique pentanuclear $[(UO_2)_5O_2(OH)_2]$ discrete motif which fills a nuclearity gap among uranyl SBUs. The addition of copper(II) or nickel(II) ions and bipyrimidine ligands yields one-dimensional assemblies displaying different stoichiometries and topologies, evidencing once more the versatility of this system. All these results show that a rich structural chemistry is open to investigation in the $UO_2$−sulfonate system, which, as the thoroughly investigated $UO_2$−phosphonate system, is of interest for the synthesis of novel uranyl−organic polymers and heterometallic complexes.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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