Actinide Structural Studies. Part 7.[1] The Crystal and Molecular Structures of (2,2′-Bipyridyl)dinitratodioxo-uranium(VI) and -neptunium(VI), and Diacetato-(2,2′-bipyridyl)dioxo-uranium(VI) and -neptunium(VI)†

Nathaniel W. Alcock* and David J. Flanders
Department of Chemistry, University of Warwick, Coventry CV4 7AL
David Brown
Building 220, Chemistry Division, A.E.R.E. Harwell, Didcot, Oxfordshire OX11 0RA

The crystal structures of the title compounds, $[MO_2(bipy)(NO_3)_2]$ [M = U (**1**) or Np (**2**)] and $[MO_2(bipy)(CH_3COO)_2]$ [M = U (**3**) or Np (**4**)] (bipy = 2,2′-bipyridyl) have been determined using *X*-ray diffraction techniques. Complexes (**1**) and (**2**) are isomorphous and isostructural crystallising in the monoclinic system, space group *C*2/*c*; (**3**) and (**4**) are also isomorphous and isostructural, crystallising in the monoclinic system, space group $P2_1/n$. All four complexes exhibit hexagonal-bipyramidal co-ordination about the central metal atom. The M–O bond lengths in the MO_2^{2+} cations are 1.763(13) (**1**), 1.728(7) (**2**), 1.770(8) (mean) (**3**), and 1.729(10) Å (mean) (**4**). The bidentate oxy-anions have M–O distances of 2.472(8)—2.494(13) Å in (**1**) and (**2**), and 2.429(9)—2.476(9) Å in (**3**) and (**4**). For the bidentate 2,2′-bipyridyl group the M–N distances are 2.578(13) (**1**), 2.564(9) (**2**), 2.631(10) and 2.642(9) (**3**), and 2.835(13) and 2.842(13) Å (**4**). This anomalous increase in the M–N distance between complexes (**3**) and (**4**) is attributed to overcrowding around the NpO_2^{2+} ion.

A number of 2,2′-bipyridyl (bipy) complexes of dioxouranium(VI) have been reported,[2] but the available structural information is based only on i.r. spectral analysis. No bipy complexes of dioxoneptunium(VI) have been prepared, while actinyl–nitrogen bonds in general have hardly been examined. It was therefore of interest to prepare complexes of this type and examine their structures in order that changes arising from the variation of actinide element may be evaluated. We now report the crystal structures of $[UO_2(bipy)(NO_3)_2]$ (1), $[NpO_2(bipy)(NO_3)_2]$ (2), $[UO_2(bipy)(CH_3COO)_2]$ (3), and $[NpO_2(bipy)(CH_3COO)_2]$ (4). A preliminary report has been published.[3]

Experimental

Preparations.—Complex (1) was prepared by the method of Balakrishnan *et al.*[4] and recrystallised from methanol. Complex (2) was prepared by adding an ethanol solution (1 cm^3) of 2,2′-bipyridyl (0.37 mmol) to an ethanol solution (1 cm^3) of freshly prepared neptunyl(VI) nitrate (0.25 mmol).[5] Crystals precipitated rapidly on standing. Complex (3) was prepared by the method of Markov and Tsapkin[6] and recrystallised from methanol. Complex (4) was prepared by adding a hot aqueous solution (1 cm^3) of 2,2′-bipyridyl (0.26 mmol) to a warm aqueous solution (1 cm^3) of freshly prepared sodium tris(acetato)-dioxoneptunate(1 −) (0.25 mmol).[7] The solid product formed slowly, and the supernatant was pipetted off after centrifugation. The product was washed in ice-cold water to remove sodium acetate, and recrystallised from methanol.

Suitable crystals of all four complexes were mounted on quartz fibres, with those of (2) and (4) encapsulated in Lindemann glass capillaries. The crystals of complexes (2) and (4) were handled in a glove-box to afford protection from the α-radiation of ^{237}Np.

Data Collection and Structural Refinement.—Reflection data were collected using a Syntex $P2_1$ automatic four-circle diffractometer, with the temperature controlled by the L.T.-1 attachment in the case of complex (2). Accurate unit-cell parameters were obtained from least-squares calculations based on the positions of 15 high-angle reflections. Three standard reflections were measured every 200 reflections, and showed slight changes during data collection; the data were rescaled to allow for this; Mo-K_α radiation (λ = 0.710 69 Å) was used throughout. The θ—2θ scan mode was used and the scan rate varied from 2.0 to 29.3° min^{-1}, depending on the intensity of a 2-s pre-scan. Lorentz, polarisation, and absorption corrections were applied, the last with the program ABSCOR.[8] The scattering factors used were corrected for anomalous dispersion.[9] Calculations were carried out with the *X*-RAY 76 system[10] on a Burroughs B6700 computer. The crystal data and data-collection conditions for each compound are given in Table 1.

For complex (1) the systematic absences, $hkl(h + k \neq 2n)$ and $h0l(l \neq 2n)$, indicated two possible space groups, *C*2/*c* or *Cc*. The former was chosen and the uranium atom was placed in special position 4e with two-fold site symmetry, based on examination of a Patterson synthesis, and the non-hydrogen atoms were located on successive Fourier syntheses. The structure of complex (2) was refined starting from the atomic positions of (1). The systematic absences $0k0(k \neq 2n)$ and $h0l(h + l \neq 2n)$ in the data collected for complex (3) indicated the space group $P2_1/n$ (a non-standard setting of $P2_1/c$). The positions of (1). The systematic absences $0k0(k \neq 2n)$ and $h0l$ three-dimensional Patterson map, with the non-hydrogen atoms located on successive Fourier syntheses. The structure of complex (4) was refined starting from the atomic positions of the uranyl(VI) analogue (3). Final refinement of the non-hydrogen atoms with anisotropic thermal parameters was by least-squares methods. For complex (1) unit weights were used. For (2)—(4) a weighting scheme of the form $w = XY$ where X = 1.0 or $(\sin\theta/\lambda)/A$ for $(\sin\theta/\lambda) \geqslant A$ or $B/(\sin\theta/\lambda)$ for $(\sin\theta/\lambda) \geqslant B$ and Y = 1.0 or F_o/C for $F_o \leqslant C$ or D/F_o for $F_o \geqslant D$ was employed (constants in Table 1). These were shown to be satisfactory by a weight analysis. The final *R* values are given in Table 1.

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† *Supplementary data available* (No. SUP 56163, 5 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Crystal data and data collection conditions

Compound	(1)	(2)	(3)	(4)
Formula	$C_{10}H_8N_4O_8U$	$C_{10}H_8N_4NpO_8$	$C_{14}H_{14}N_2O_6U$	$C_{14}H_{14}N_2NpO_6$
M	550.24	549.20	544.32	543.28
Space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$
a/Å	13.370(2)	13.365(4)	7.949(1)	7.927(1)
b/Å	9.977(3)	9.935(5)	19.032(5)	19.126(4)
c/Å	10.538(2)	10.451(2)	10.602(3)	10.604(2)
β/°	99.81(1)	99.95(2)	95.66(2)	95.87(2)
U/Å^3	1 385.1(5)	1 366.8(8)	1 596.1(7)	1 599.2(6)
D_c/g cm^{-3}	2.64	2.67	2.26	2.26
μ(Mo-K_α)/cm^{-1}	111.6	49.79	96.8	42.43
Crystal size/mm	0.12 × 0.08 × 0.30	0.17 × 0.02 × 0.28	0.36 × 0.11 × 0.10	0.42 × 0.12 × 0.12
Transmission factor: max.	0.52	0.90	0.66	0.81
min.	0.31	0.48	0.50	0.70
Temperature, θ_c/°C	16	−100	16	16
Scan range about $K_{\alpha_1} - K_{\alpha_2}$/°	−1.0 to 1.1	±1.1	−1.0 to +1.1	−1.0 to 1.1
Reflections: collected	1 367	1 358	3 072	3 160
observed [$I/\sigma(I) \geqslant 3.0$]	1 108	1 083	1 821	1 936
Weighting constants: A, B		0.20, 0.60	0.37, 0.37	0.05, 0.99
C, D		50.0, 180.0	70.0, 180.0	24.0, 200.0
Final R value	0.026	0.036	0.036	0.035

Details common to all complexes: monoclinic, $Z = 4$.

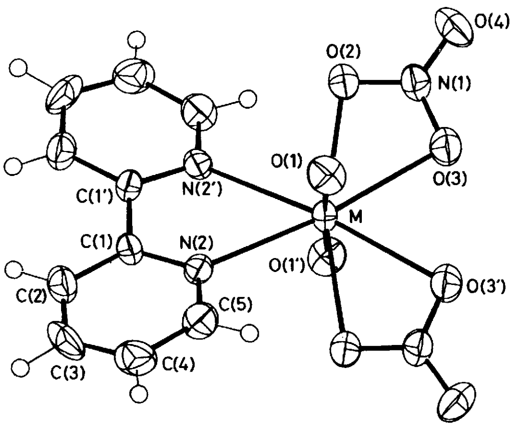

Figure 1. The $[MO_2(bipy)(NO_3)]$ (M = U or Np) molecule showing atomic numbering

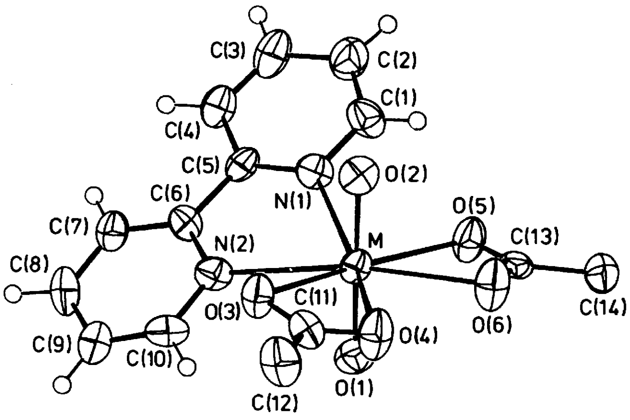

Figure 2. The $[MO_2(bipy)(CH_3COO)_2]$ (M = U or Np) molecule showing atomic numbering

Hydrogen atoms were inserted at calculated positions, in each case, with fixed isotropic thermal parameters, $B = 5.0$ Å^2, and were not refined.

Final atomic co-ordinates are given in Table 2, selected bond distances and angles in Tables 3 and 4, and least-squares planes for the bipyridyl rings and the equatorial ligand rings around the metal atoms in Tables 5 and 6. The numbering scheme for complexes (**1**) and (**2**) is given in Figure 1 and that for (**3**) and (**4**) in Figure 2. The packing of (**1**) and (**2**) viewed obliquely is shown in Figure 3 and of (**3**) and (**4**), viewed down a, in Figure 4.

Discussion

Of the four structures described in this paper the two nitrate and the two acetate complexes are isomorphous and isostructural. All four exhibit distorted hexagonal-bipyramidal geometry with the central metal atom co-ordinated to six oxygen atoms (two axial and four equatorial) and two nitrogen atoms. A comparison of the molecular plots in Figures 1 and 2 shows the marked similarities between the two pairs of complexes. The differences in the axial metal–oxygen distances between the compounds are typical of the actinide contraction found on substituting Np for U. The M–O (MO_2^{2+}) distance contracts from 1.763(13) to 1.728(7) Å in the nitrates and from 1.770(8) (mean) to 1.729(10) (mean) Å in the acetates, a mean contraction of 0.038 Å, similar to those found in complexes with phosphine oxide ligands[11] where M–O (MO_2^{2+}) bond lengths decrease by 0.025 and 0.028 Å. The M–O (nitrate) bond distances show a very slight contraction from 2.49(1) and 2.48(1) Å to 2.48(1) and 2.47(1) Å and the M–O (acetate) bond lengths apparently increase slightly from 2.450(9) (mean) to 2.455(9) (mean) Å, although neither of these changes is statistically significant. Both M–O bonds are comparable with the distances in other uranyl nitrate and acetate compounds.[12]

Uranium-nitrogen bond lengths have been found previously in the rather wide range of 2.47—2.66 Å[13,14] which covers the values found in complexes (**1**) and (**3**) [2.578(13), 2.642(9), and 2.631(10) Å]. The substitution of Np for U in (**2**) causes a small decrease in the M–N bond length as expected from the contractions in the M–O bond distances. However there is a striking anomaly in the change in the M–N bond lengths in the acetate complexes. The substitution of Np for U causes an *increase* in the bond length of no less than 0.20 Å [from 2.642(9) and 2.631(10) Å to 2.842(13) and 2.835(13) Å]. Examination of

Table 2. Atomic co-ordinates (× 10^4), with standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Complex (**1**)				Complex (**2**)			
U	0.0	652.7(8)	2 500.0	Np	0.0	655.9(6)	2 500.0
O(1)	745(8)	619(12)	4 050(9)	O(1)	728(6)	625(9)	4 036(7)
O(2)	1 663(8)	306(10)	1 779(10)	O(2)	1 666(6)	326(7)	1 796(7)
O(3)	842(9)	−1 473(11)	2 062(12)	O(3)	840(7)	−1 478(8)	2 084(9)
O(4)	2 327(9)	−1 636(12)	1 478(12)	O(4)	2 328(7)	−1 625(9)	1 486(8)
N(1)	1 643(10)	−961(12)	1 754(12)	N(1)	1 646(8)	−959(9)	1 770(9)
N(2)	566(9)	2 863(12)	1 570(11)	N(2)	567(7)	2 854(9)	1 556(8)
C(1)	355(11)	4 066(13)	2 028(14)	C(1)	346(8)	4 074(10)	2 026(9)
C(2)	764(13)	5 244(15)	1 631(17)	C(2)	771(9)	5 256(10)	1 629(11)
C(3)	1 380(14)	5 185(17)	707(18)	C(3)	1 388(10)	5 204(12)	711(12)
C(4)	1 540(13)	3 974(18)	156(18)	C(4)	1 546(9)	3 965(12)	161(12)
C(5)	1 122(13)	2 835(16)	612(15)	C(5)	1 127(9)	2 837(12)	597(10)
Complex (**3**)				Complex (**4**)			
U	2 197.9(6)	1 696.4(2)	3 407.4(4)	Np	2 204.5(7)	1 690.6(2)	3 418.2(5)
O(1)	4 434(10)	1 723(5)	3 447(8)	O(1)	4 379(13)	1 730(6)	3 476(8)
O(2)	−29(10)	1 658(5)	3 324(8)	O(2)	6(12)	1 658(5)	3 347(8)
O(3)	1 945(14)	2 256(4)	5 471(9)	O(3)	1 934(15)	2 253(5)	5 474(9)
O(4)	2 229(13)	2 945(4)	3 886(8)	O(4)	2 228(16)	2 948(5)	3 886(8)
O(5)	2 312(13)	1 319(4)	1 184(8)	O(5)	2 340(14)	1 307(4)	1 200(8)
O(6)	1 962(10)	2 431(5)	1 514(8)	O(6)	1 950(15)	2 421(5)	1 533(9)
N(1)	1 601(12)	333(5)	3 223(10)	N(1)	1 573(15)	343(5)	3 218(10)
N(2)	3 190(13)	871(5)	5 328(10)	N(2)	3 181(15)	871(5)	5 334(10)
C(1)	722(18)	90(6)	2 167(13)	C(1)	729(20)	86(7)	2 144(13)
C(2)	167(20)	−612(7)	2 005(14)	C(2)	148(21)	−593(7)	2 011(13)
C(3)	494(20)	−1 066(7)	3 032(14)	C(3)	483(22)	−1 055(7)	3 017(16)
C(4)	1 347(17)	−819(6)	4 126(12)	C(4)	1 320(20)	−801(7)	4 125(14)
C(5)	1 866(15)	−108(6)	4 184(11)	C(5)	1 865(16)	−110(6)	4 202(11)
C(6)	2 822(16)	170(6)	5 349(12)	C(6)	2 864(16)	175(6)	5 363(12)
C(7)	3 438(20)	−249(7)	6 351(13)	C(7)	3 422(19)	−245(7)	6 392(13)
C(8)	4 436(16)	54(6)	7 368(12)	C(8)	4 449(21)	49(8)	7 385(14)
C(9)	4 839(19)	749(8)	7 311(13)	C(9)	4 794(20)	757(8)	7 345(14)
C(10)	4 165(14)	1 141(6)	6 314(11)	C(10)	4 189(18)	1 147(7)	6 321(13)
C(11)	2 050(16)	2 876(6)	5 040(12)	C(11)	2 038(18)	2 866(7)	5 040(13)
C(12)	1 926(20)	3 503(6)	5 905(13)	C(12)	1 949(22)	3 497(7)	5 894(13)
C(13)	2 203(16)	1 940(6)	778(12)	C(13)	2 187(17)	1 925(6)	777(12)
C(14)	2 408(19)	2 091(8)	−613(13)	C(14)	2 375(22)	2 089(7)	−624(12)

Table 3. Bond lengths (Å) and bond angles (°) with standard deviations in parentheses for $[MO_2(bipy)(NO_3)_2]$ [M = U (**1**) or Np (**2**)] (primed atoms are related to unprimed by a two-fold axis)

	(**1**)	(**2**)		(**1**)	(**2**)
(*i*) Around M			(*iii*) Bipyridyl groups		
M–O(1)	1.763(13)	1.728(7)	N(2)–C(1)	1.34(2)	1.36(1)
M–O(2)	2.494(13)	2.484(6)	N(2)–C(5)	1.35(2)	1.35(2)
M–O(3)	2.481(12)	2.472(8)	C(1)–C(1′)	1.49(2)	1.47(2)
M–N(2)	2.578(13)	2.564(9)	C(1)–C(2)	1.39(2)	1.40(1)
			C(2)–C(3)	1.38(3)	1.37(2)
(*ii*) Nitrate groups			C(3)–C(4)	1.37(3)	1.39(2)
N(1)–O(2)	1.264(15)	1.277(12)	C(4)–C(5)	1.39(3)	1.37(2)
N(1)–O(3)	1.278(19)	1.288(14)			
N(1)–O(4)	1.210(19)	1.203(14)			
(*i*) Around M			(*ii*) Nitrate groups		
O(1)–M–O(1′)	177.8(6)	177.9(4)	O(2)–N(1)–O(3)	114(1)	114(1)
O(1)–M–O(2)	83.5(4)	83.3(3)	O(2)–N(1)–O(4)	123(1)	123(1)
O(1′)–M–O(2)	96.2(4)	96.4(3)	O(3)–N(1)–O(4)	123(1)	123(1)
O(1)–M–O(3)	87.3(5)	87.0(4)			
O(1′)–M–O(3)	90.8(5)	91.2(4)	(*iii*) Bipyridyl groups		
O(1)–M–N(2)	102.3(5)	102.5(3)	C(5)–N(2)–C(1)	118(1)	117(1)
O(1′)–M–N(2)	79.7(5)	79.3(3)	N(2)–C(1)–C(1′)	122(1)	116(1)
O(2)–M–O(3)	50.8(4)	51.5(3)	N(2)–C(1)–C(2)	116(1)	121(1)
O(2)–M–N(2)	70.6(4)	70.1(3)	C(2)–C(1)–C(1′)	122(1)	122(1)
O(3)–M–O(3′)	62.5(4)	61.9(3)	C(1)–C(2)–C(3)	119(1)	120(1)
N(2)–M–N(2′)	62.4(4)	63.2(3)	C(2)–C(3)–C(4)	119(2)	118(1)
			C(3)–C(4)–C(5)	118(2)	119(1)
			C(4)–C(5)–N(2)	123(1)	123(1)

Table 4. Bond lengths (Å) and angles (°) with standard deviations in parentheses for $[MO_2(bipy)(CH_3COO)_2]$ [M = U (**3**) or Np (**4**)]

	(3)	(4)
(*i*) Around M		
M–O(1)	1.774(8)	1.720(10)
M–O(2)	1.765(8)	1.737(10)
M–O(3)	2.459(9)	2.460(9)
M–O(4)	2.429(9)	2.455(9)
M–O(5)	2.475(9)	2.476(9)
M–O(6)	2.438(9)	2.430(9)
M–N(1)	2.642(9)	2.842(13)
M–N(2)	2.631(10)	2.835(13)
(*ii*) Acetate groups		
C(11)–C(12)	1.514(8)	1.514(20)
C(11)–O(3)	1.271(9)	1.264(16)
C(11)–O(4)	1.252(9)	1.259(17)
C(13)–C(14)	1.526(8)	1.542(19)
C(13)–O(5)	1.257(9)	1.265(15)
C(13)–O(6)	1.245(9)	1.268(16)
(*iii*) Bipyridyl groups		
N(1)–C(1)	1.34(2)	1.35(1)
C(1)–C(2)	1.41(2)	1.38(1)
C(2)–C(3)	1.39(2)	1.40(2)
C(3)–C(4)	1.37(2)	1.38(2)
C(4)–C(5)	1.41(2)	1.39(2)
C(5)–N(1)	1.32(2)	1.36(2)
C(5)–C(6)	1.48(2)	1.50(2)
C(6)–N(2)	1.37(2)	1.36(2)
C(6)–C(7)	1.38(2)	1.39(2)
C(7)–C(8)	1.40(2)	1.38(2)
C(8)–C(9)	1.36(2)	1.38(2)
C(9)–C(10)	1.36(2)	1.36(2)
C(10)–N(2)	1.34(1)	1.36(2)
(*i*) Around M		
O(1)–M–O(2)	178.3(3)	179.3(4)
O(3)–M–O(4)	52.5(3)	52.6(3)
O(4)–M–O(6)	67.0(3)	66.5(3)
O(5)–M–O(6)	52.3(3)	52.9(3)
N(1)–M–N(2)	60.6(3)	61.0(3)
N(1)–M–O(5)	70.6(3)	70.1(3)
N(2)–M–O(3)	67.3(3)	67.7(3)
O(1)–M–O(3)	97.9(4)	97.3(4)
O(1)–M–O(4)	88.7(4)	87.9(5)
O(1)–M–O(5)	84.2(4)	84.6(4)
O(1)–M–O(6)	89.9(3)	90.1(4)
O(1)–M–N(1)	101.6(4)	103.1(4)
O(1)–M–N(2)	77.0(4)	77.5(4)
(*ii*) Acetate groups		
C(12)–C(11)–O(3)	120.2(4)	120.8(12)
C(12)–C(11)–O(4)	122.0(4)	120.0(12)
O(3)–C(11)–O(4)	117.8(6)	119.2(12)
C(14)–C(13)–O(5)	119.8(4)	121.2(12)
C(14)–C(13)–O(6)	120.2(4)	119.4(11)
O(5)–C(13)–O(6)	120.0(6)	119.3(12)
(*iii*) Bipyridyl groups		
N(1)–C(1)–C(2)	123.9(12)	123.9(12)
C(1)–C(2)–C(3)	117.4(13)	119.0(13)
C(2)–C(3)–C(4)	119.1(12)	117.9(13)
C(3)–C(4)–C(5)	119.0(11)	120.3(13)
C(4)–C(5)–N(1)	123.4(11)	122.3(11)
C(4)–C(5)–C(6)	120.1(10)	122.0(11)
N(1)–C(5)–C(6)	116.4(10)	115.7(10)
N(2)–C(6)–C(7)	121.1(11)	122.7(11)
N(2)–C(6)–C(5)	115.3(10)	115.0(10)
C(5)–C(6)–C(7)	123.3(11)	122.3(11)
C(6)–C(7)–C(8)	119.2(11)	118.6(12)
C(7)–C(8)–C(9)	118.9(11)	118.5(13)
C(8)–C(9)–C(10)	119.4(12)	120.4(13)
C(9)–C(10)–N(2)	123.2(11)	122.2(12)
C(10)–N(2)–C(6)	118.0(10)	117.4(10)

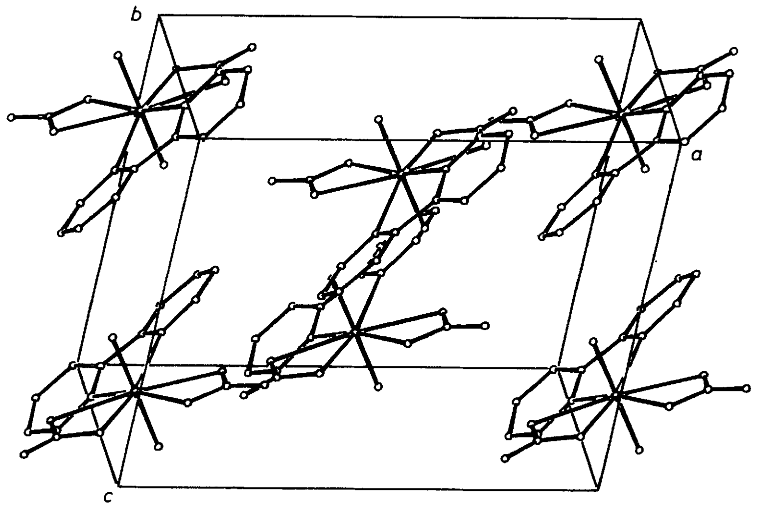

Figure 3. The packing of $[MO_2(bipy)(NO_3)_2]$ viewed obliquely

Table 5. Deviations (Å) from mean planes for $[\mathrm{MO_2(bipy)(NO_3)_2}]$ [M = U (**1**) or Np (**2**)] (primed atoms are related to unprimed by a two-fold axis, starred atoms define planes)

Plane 1	(1)	(2)
M*	0.000	0.000
O(2)*	0.234	0.237
O(3)*	0.054	0.066
N(2)*	−0.526	−0.540
O(2′)*	−0.234	−0.237
O(3′)*	−0.054	−0.066
N(2′)*	0.526	0.540
Plane 2		
M*	0.000	0.000
N(2)*	−0.027	−0.025
C(1)*	0.049	0.046
C(1′)*	−0.049	−0.046
N(2′)*	0.027	0.025
Plane 3		
O(2)*	0.001	0.001
O(3)*	0.001	0.001
O(4)*	0.002	0.001
N(1)*	−0.004	−0.003
Line 4		
O(1)*	0.011	0.010
M*	0.022	0.020
O(1′)*	0.011	0.010
Angles (°) between plane normals and line		
1:2	21.98	22.63
1:3	7.09	6.48
1:4	0.93	1.09
2:3	29.00	29.00
2:4	21.05	21.54
3:4	8.02	7.54

the cell constants (in Table 1) also shows a surprising deviation. The normal expectation, on replacing U by Np, is of a slight contraction corresponding to the decrease in ionic radius between the two elements, as is found for the nitrates. In the case of the acetate complexes the unit-cell volume of the neptunyl compound is significantly larger than that of the uranyl analogue, and this change arises specifically from an increase of 0.1 Å in the *b* axis length. The packing of the acetate compounds (Figure 4) shows that this axial length expansion is caused by the increases in M–N bond lengths because these are aligned broadly parallel to *b*.

Evidence for the cause of this anomalous expansion may be found by examining the equatorial non-bonded contacts (Table 7). These show that the bipyridyl ligand has a relatively large bite (2.67 Å), and that the bite of the acetate group is compressed below the expected value (about 2.21 Å). The Table also shows evidence of inter-ligand compression, particularly in the very short O ··· O contacts between the nitrate or acetate groups compared to an unconstrained value of 2.7—2.8 Å. The compressions have resulted in considerable distortions of the molecules from the ideal geometry of a precisely planar equatorial set of ligands. The co-ordinating ligand atoms are substantially displaced out of the mean equatorial plane (by up to 0.6 Å) as can be seen in Tables 5 and 6. The oxy-anions are rotated about the N–O or C–C bond so that the co-ordinating oxygen atoms are twisted alternately above and below the equatorial plane. The 2,2′-bipyridyl ligands are twisted in two ways, first by twisting of the whole molecule about the centre of the 1–1′ C–C bond in the direction that increases the N ··· O contact distance (bipyridyl twist) and secondly by rotation of the two rings of the bipyridyl group about this bond (increasing the bipyridyl dihedral angle). These displacements are shown

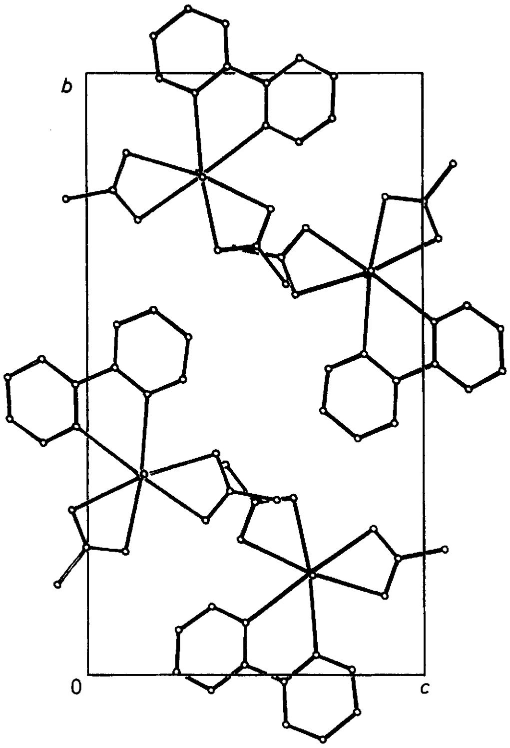

Figure 4. The packing of $[\mathrm{MO_2(bipy)(CH_3COO)_2}]$ viewed down the *a* axis

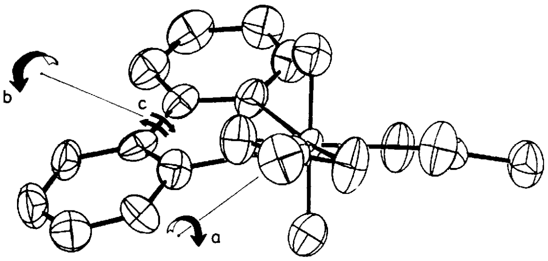

Figure 5. Distortions in the structure of $[\mathrm{MO_2(bipy)X_2}]$ (M = U or Np, X = $\mathrm{NO_3^-}$ or $\mathrm{CH_3COO^-}$)

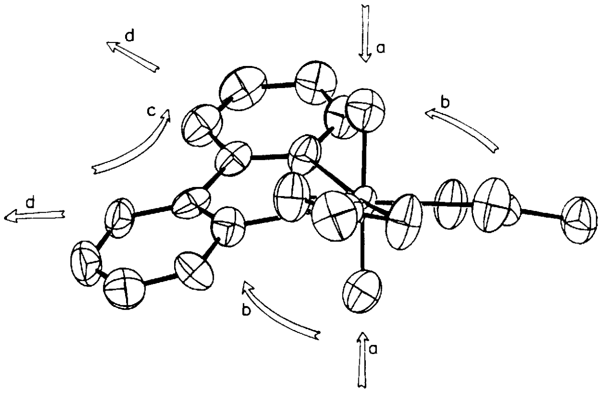

Figure 6. The sequence of reactions on compressing the $[\mathrm{MO_2(bipy)(CH_3COO)_2}]$ complex by replacing U by Np

Table 6. Deviations (Å) from mean planes for $[MO_2(bipy)(CH_3COO)_2]$ [M = U (**3**) or Np (**4**)] (starred atoms define planes)

Plane 1	(3)	(4)
M*	−0.004	0.004
O(3)*	−0.340	−0.339
O(4)*	0.046	0.049
O(5)*	0.244	0.261
O(6)*	−0.004	−0.018
N(1)*	−0.533	−0.548
N(2)*	0.591	0.591
Plane 2		
N(1)*	0.000	0.000
C(5)*	0.000	0.000
C(4)*	0.000	0.000
N(2)	−0.013	−0.070
C(6)	0.057	0.047
C(7)	0.284	0.201
Plane 3		
N(1)	0.337	0.155
C(5)	0.127	0.001
C(4)	0.075	−0.106
N(2)*	0.000	0.000
C(6)*	0.000	0.000
C(7)*	0.000	0.000

Plane 4	(3)	(4)
M*	−0.036	−0.028
N(1)*	0.065	0.058
C(5)*	−0.057	−0.059
C(6)*	−0.011	0.007
N(2)*	0.039	0.021
Plane 5		
O(3)*	0.000	0.000
O(4)*	0.000	0.000
C(11)*	0.000	0.000
C(12)	−0.025	0.010
Plane 6		
O(5)*	0.000	0.000
O(6)*	0.000	0.000
C(13)*	0.000	0.000
C(14)	0.032	0.074
Line 7		
O(1)*	0.009	0.003
M*	0.018	0.007
O(2)*	0.009	0.003

Angles (°) between plane normals and line

	(3)	(4)		(3)	(4)
1:2	26.13	27.65	3:4	6.76	2.62
1:3	32.27	28.67	3:5	41.29	37.95
1:4	25.59	26.13	3:6	43.75	38.88
1:5	11.10	11.21	3:7	56.88	60.55
1:6	11.49	10.32	4:5	34.52	35.34
1:7	89.14	89.07	4:6	37.08	36.36
2:3	9.74	6.62	4:7	63.55	63.08
2:4	5.75	5.86	5:6	7.82	9.02
2:5	33.54	35.42	5:7	79.46	79.03
2:6	37.33	37.96	6:7	79.37	80.53
2:7	63.02	61.47			

Table 7. Equatorial non-bonded contacts (Å)

(*a*) Intra-ligand 'bites'		U	Np	Average
N···N	Nitrate	2.67(2)	2.69(2)	2.68
	Acetate	2.66(1)	2.66(1)	2.66
O···O	Nitrate	2.13(2)	2.15(1)	2.14
	Acetate	2.16(1) 2.17(1)	2.18(1) 2.19(1)	2.175
(*b*) Contacts between ligands				
N···O	Nitrate	2.93(2)	2.90(1)	
	Acetate	2.83(1) 2.96(1)	2.83(1) 2.93(1)	
O···O	Nitrate	2.57(2)	2.54(1)	
	Acetate	2.69(1)	2.68(1)	

Table 8. Distortions (°) in the equatorial groups

	Nitrate		Acetate	
	U	Np	U	Np
(*a*) Oxy-anion twist (dihedral angle between anion and mean equatorial plane)	7.0	6.5	11.3 (average)	10.8 (average)
(*b*) Bipyridyl twist (dihedral angle between mean N–C–C–N plane, and mean equatorial plane)	22.0	22.7	25.6	26.1
(*c*) Bipyridyl dihedral angle (between two rings of bipyridyl molecule)	12.7	13.2	−8.3	−8.0

graphically in Figure 5, and Table 8 shows that the extent of these distortions varies between the nitrates and the acetates although the members of each pair are almost identical. The biggest difference is in the bipyridyl dihedral angle. For the nitrates this is +13°, in the sense that increases the distance of the two nitrogen atoms from the equatorial plane (*i.e.* reinforcing the bipyridyl twist), while for the acetates it is −8°, reversing the bipyridyl twist. The bipyridyl group is twisted overall through a greater angle in the acetate complexes, in compensation for this difference in dihedral angle, so that the nitrogen atoms are displaced out of the equatorial plane by similar amounts in the acetates and the nitrates.

The most important steric constraint affecting the deformation of the equatorial girdle seems to be repulsions involving the oxygen atoms of the MO_2^{2+} groups, which tend to keep the equatorial atoms coplanar. The distances from these atoms to the equatorial O and N atoms (Table 9) have a very constant

Table 9. Distances (Å) from actinyl oxygen atoms to equatorial ligand atoms

		U	Np
N···O	Nitrate	2.85(2)—3.42(2)	2.81(1)—3.39(1)
	Acetate	2.82(1)—3.50(1)	2.80(1)—3.46(1)
O···O	Nitrate	2.89(2)—3.22(2)	2.86(1)—3.18(1)
	Acetate	2.87(1)—3.20(1)	2.83(1)—3.18(1)

minimum of about 2.8 Å. Those of the NpO_2^{2+} compounds are consistently smaller than in the UO_2^{2+} compounds, with the values for the acetates smaller than for the nitrates. In the uranyl acetate complex these steric factors have reached a critical level and the replacement of U by Np causes considerable deformation of the molecule which depends on the relative bond strengths. These must be in the order: M=O (MO_2^{2+} group) $\gg$ M–O (equatorial) > M–N (equatorial). The difference in strength between M–O (equatorial) and M–N (equatorial) has been explained by the relative softness of the N atom.[15]

Thus, on replacing U by Np (Figure 6), (*a*) the MO_2^{2+} groups contract by a constant amount irrespective of the equatorial co-ordination. The equatorial bonds would also be expected to shrink, but as seen above, this cannot take place for the acetate. The first consequence of the compression (*a*) is to reduce the $O(MO_2^{2+})\cdots O$(equatorial) distance. To remove this stress, (*b*) the acetate or nitrate twist is slightly reduced. This in its turn decreases the O(equatorial)···N distances. This is relieved (*c*) by increasing the bipyridyl twist, and the dihedral angle. However, this decreases the $O(MO_2^{2+})\cdots N$ distances. Then, in the acetate the two sets of oxygen atoms (axial and equatorial) act as pincers and (*d*) squeeze out the nitrogen ligand, whose N–M bonds are the weakest and longest in the complex.

Figure 6 graphically summarises the whole process showing that the steric strain in the complex effectively causes it to behave like a coiled spring, which on compression at one point distorts at another. In this process, by a detailed comparison of the four compounds studied, the essentially static crystallographic results can become a dynamic 'moving picture.'

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