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A Unique Expansion on Substituting Neptunium for Uranium in an Actinyl Complex

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Crystal structure determinations on the four complexes MO_2 (4,4-bipyridyl)X_2 with M = U, Np; X = nitrate, acetate, show the normal contraction in M–ligand distances on replacing U by Np, when X = nitrate. When X = acetate, the Np complex has a larger unit cell volume and longer Mp–N distances (U–N, 2.636(7)); Np–N, 2.838(10) Å). This is explained by overcrowding caused by the large bite bipyridyl ligand.

We have recently undertaken a comparison between UO_2^{2+} and NpO_2^{2+} compounds, in which the additional ligands have been oxygen donors [1]. This has now been extended to complexes containing nitrogen donor atoms, including the four described here:

$MO_2(bipy)(NO_3)_2$ and $MO_2(bipy)(O_2CCH_3)_2$ with M = U, Np; bipy = 4,4-bipyridyl.

These exist as isomorphous pairs (Table I), and examination of the cell constants shows a surprising trend. The expectation on replacing U by Np is a slight contraction, corresponding to the decrease in ionic radius between the two elements, and this appears for the nitrate. However, the unit cell volume for the neptunyl acetate is significantly larger than for the uranyl acetate, and this change arises specifically from an increase of 0.1 Å in the *b* axis length.

Figure 1 shows an overall view of the molecules, which have the expected six equatorial atoms around

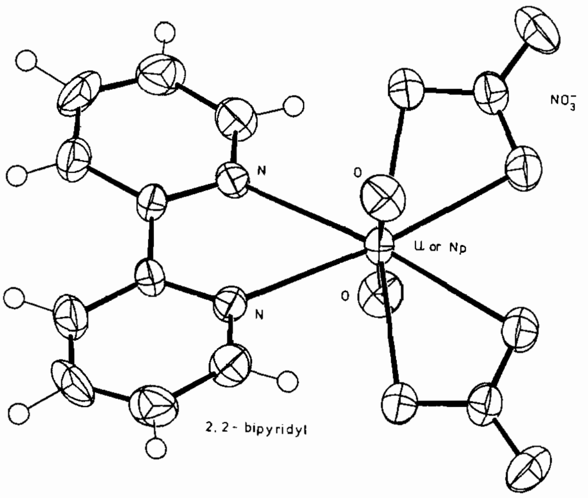

Fig. 1. View of $MO_2(bipy)(NO_3)_2$, (M = U, Np). The acetate complexes are superficially identical to the nitrates apart from the replacement of NO_3^- by $CH_3CO_2^-$.

TABLE I. Cell Constants (Diffractometer Data at 16 °C, Corrected for Absorption, Refined on Reflections with $I/\sigma(I) \geq 3.0$).

	$MO_2(bipy)(NO_3)_2$		$MO_2(bipy)(O_2CCH_3)_2$	
M	U	Np	U	Np
Space Group	C2/c	C2/c	$P2_1/n$	$P2_1/n$
Z	4	4	4	4
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(3)	10.602(2)	10.604(2)
β/°	99.81(1)	99.95(2)	95.66(2)	95.87(2)
U/Å^3	1385.1	1366.8	1596.1	1599.2
R	0.026	0.036	0.036	0.035

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TABLE II. Metal–Ligand Distances (A).

(a) MO_2^{2+} Groups		U	Np	diff. (U–Np)
Acetate	M–O	1.769(6)	1.728(7)	0.041
Nitrate	M–O	1.763(13)	1.728(7)	0.035
(b) Equatorial Ligands (avg.)				
Nitrate	M–O	2.488(9)	2.478(6)	0.010
	M–N	2.578(13)	2.564(9)	0.014
Acetate	M–O	2.450(9)	2.455(9)	−0.005
	M–N	2.636(7)	2.838(10)	−0.202

linear actinyl groups. Consideration of the metal-ligand distances (Table II) shows a typical actinide contraction in the MO_2^{2+} groups, of about 0.04 Å, not significantly larger than the 0.03 Å found in phosphine oxide complexes [1]. The equatorial nitrate ligands also show contractions, though rather smaller, but the abnormalities appear for the acetate. Here, the M–O distances are identical within experimental error, but the Np–N distance is larger than the U–N distance, by no less than 0.20 Å. A consideration of the packing diagram (Fig. 2) for the acetates confirms that this expansion underlies the abnormal volume and *b* axis changes, because the M–N bonds are aligned broadly parallel to *b*.

In looking for the cause of the expansion, the equatorial non-bonded contacts are significant (Table III). These involve first the ligand 'bites'. Here it is clear (a) that the bipyridyl ligand has a relatively large bite (2.67 Å), and (b) that the acetate group bite is compressed below the expected value (about 2.21 Å). The inter-ligand contacts also show evidence of compression, in the remarkably short O- - -O contacts between the nitrate and acetate groups. Closer examination shows that even to achieve these short contacts, the molecule has undergone significant distortions from the ideal geometry of a precisely planar equatorial set of ligands. The ligand atoms are substantially displaced out of the mean equatorial plane (by up to 0.6 Å); Fig. 3 shows that these displacements arise from twisting of the ligands in three ways. First, the oxy-anions are twisted out of the equatorial plane alternately up and down. Secondly, the 4,4-bipyridyl ligands are twisted similarly, in the direction that increases the N- - -O contact distance further. Finally, the two rings of

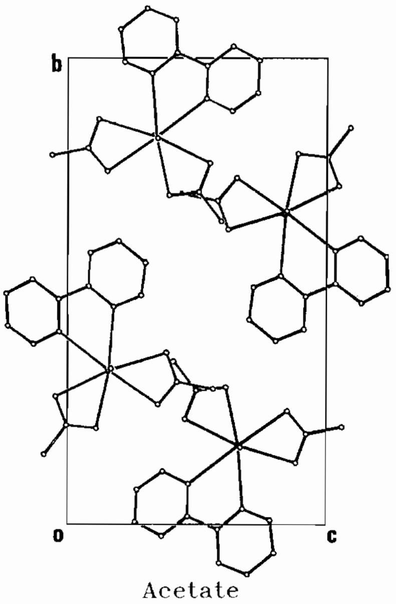

Fig. 2. Packing diagram for $MO_2(bipy)(O_2CCH_3)_2$, (M = U, Np) viewed down *a*.

TABLE III. Equatorial Non-bonded Contacts (A).

(a) Intra-ligand 'Bites'		U	Np	Avg.
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 IV. Distortions in the Equatorial Groups (°).

	Nitrate		Acetate	
	U	Np	U	Np
a Oxyanion-twist (dihedral angle between anion and mean equatorial plane)	7.0	6.5	11.3 (avg.)	10.8 (avg.)
b bipy twist (dihedral angle between mean N–C–C–N plane, and mean equatorial plane)	22.0	22.7	25.6	26.1
c bipy dihedral angle (between two bipy rings)	12.7	13.2	–8.3	–8.0

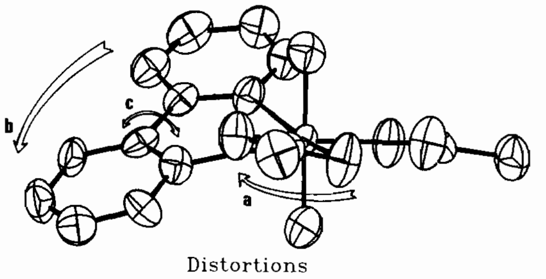

Fig. 3. Distortions in the structure of $MO_2(bipy)(X)_2$, (M = U, Np, X = NO_3^-, $CH_3CO_2^-$).

the bipyridyl group are twisted out of planarity. Table IV shows that the extent of these twists varies between the nitrates and the acetates though the members of each pair are almost identical. The biggest difference is in the bipyridyl dihedral angle. For the nitrates this is *ca.* 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. In compensation for this difference, the acetates have larger bipyridyl twist-angles, and overall the nitrogen atoms are out of plane by almost the same amounts in all four compounds. The most important steric constraint seems to be repulsions involving the oxygen atoms of the MO_2^{2+} groups. The O---O and O---N distances from these atoms (Table V) have a very constant minimum of about 2.8 Å, with the NpO_2^{2+} compounds consistently smaller than the UO_2^{2+} compounds, and the acetates smaller than the nitrates.

TABLE V. Distances from Actinyl Oxygen Atoms to Equatorial Ligand Atoms (Å).

		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)

The effect of replacing U by Np can now be seen as a dynamic process for the acetate complexes, in which the steric factors have reached a critical level. The deformability depends on the relative bond strengths, which must be in the order,

$$M = O(MO_2^{2+}\text{ group}) \gg M\text{–}O(\text{equatorial}) > M\text{–}N\ (\text{equatorial})$$

Thus, on replacing U by Np, (a) the MO_2^{2+} groups contract to a constant amount irrespective of the equatorial coordination. 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) {see Fig. 4} is to reduce the $O(MO_2^{2+})$–O (equatorial) distance. To remove this stress, (b) the acetate or nitrate twist is slightly reduced. This in its turn decreases the

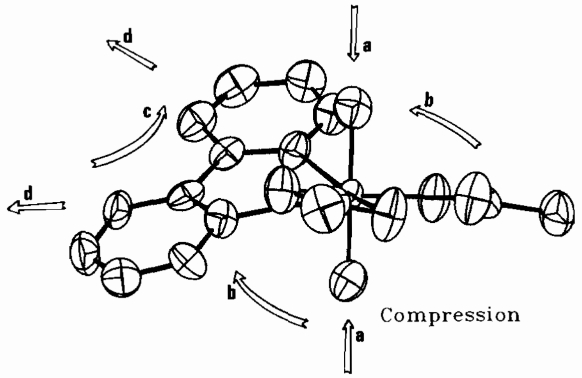

Fig. 4. The sequence of reactions on compressing the MO_2-(bipy)$(O_2CCH_3)_2$ complex by replacing U by Np.

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+})- - -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.

Effectively, the steric strain in the complex 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'.

Acknowledgements

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References

1 N. W. Alcock, M. M. Roberts and D. Brown, *J. Chem. Soc. Dalton*, 25 (1982).