

Conversion of Atmospheric Dioxygen to a μ - η^2, η^2 -Peroxo Bridge in a Dinuclear Uranium(VI) Complex

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N,N'-Ethylenebis(2-pyrrolidone) (ebpyrr) reacts with uranyl nitrate in acetonitrile, methanol, or nitromethane to form a helical chain polymer $[\text{UO}_2(\text{NO}_3)_2(\text{ebpyrr})]_n$ and, on exposure to air, also a dinuclear μ - η^2, η^2 -peroxo-bridged complex $\{[(\text{UO}_2)(\text{NO}_3)(\text{ebpyrr})]_2(\mu\text{-O}_2)\}$.

We have recently demonstrated the ability of *N,N'*-ethylenebis(2-pyrrolidone) (I, ebpyrr) and related 'extended reach' ligands to form metal complexes with unusual polymeric structures.¹ Appropriate variations in the ligand ring systems, ligand bridging units, metal ions and anions have permitted

the generation of polymeric chains, individual metallomacrocyclic rings, chains of rings, sheets of rings and three-dimensional networks. As well as their potential for taking up substrate molecules into voids and channels within these structures, an attractive feature of such systems is the

possibility of more specific substrate binding between pairs, or sets, of metal ions which form integral parts of the frameworks in these materials. The use of framework metal ions with redox capability offers the additional potential for electron transfer processes involving substrates absorbed or bound in this way. Here we demonstrate that this rationale can be applied to the conversion of dioxygen to peroxide. This is exemplified by the structural characterisation of a dinuclear U^{VI} complex formed by **1** in which dioxygen has been converted to a μ - η^2 , η^2 -peroxo-bridge.

When uranyl nitrate and **1** were mixed in acetonitrile, methanol or nitromethane, the initial solid product formed yellow hexagonal needles of stoichiometry $UO_2(NO_3)_2 \cdot (ebpyrr)$, **1**.[†] However exposure of the reaction solutions to air for several days resulted in the additional formation of orange-yellow rhombs which were found, by X-ray diffraction analysis,[‡] to have the stoichiometry $UO_2(NO_3)O(ebpyrr)$, **2**. Crystals of **2** are not formed if the solvent is purged with nitrogen and a nitrogen atmosphere maintained during the crystallisation process.

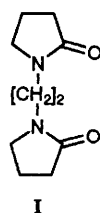
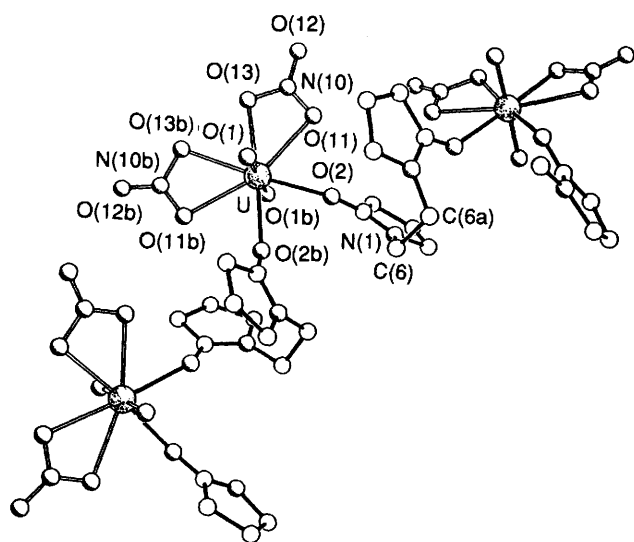
**1**

Fig. 1 Part of the helical chain present in the structure of **1** showing the hexagonal bipyramidal U coordination geometry and the *gauche* ligand linking geometry

[†] Satisfactory microanalyses were obtained.

[‡] *Crystal data* for **1**: $C_{10}H_{16}N_4O_{10}U$, hexagonal, space group $P6_522$ (or enantiomorphous $P6_122$), $a = 10.075(3)$, $c = 29.567(12)$ Å, $U = 2602$ Å³, $Z = 6$, $M = 590.3$, $D_c = 2.260$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 94$ cm⁻¹.

For **2**: $C_{20}H_{32}N_6O_{16}U_2$, monoclinic, space group $C2/c$, $a = 26.373(4)$, $b = 8.770(2)$, $c = 14.600(2)$ Å, $\beta = 118.36(2)^\circ$, $U = 2972$ Å³, $Z = 4$, $M = 1088.6$, $D_c = 2.433$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 110$ cm⁻¹.

Data for both compounds were measured on a Siemens P4/PC diffractometer with graphite monochromated (Mo-K α) radiation using ω -scans. Both structures were solved by the heavy atom method and were refined anisotropically using absorption-corrected data, to give: for **1** $R = 0.0434$, $R_w = 0.0381$ for 858 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta \leq 55^\circ$; for **2**, $R = 0.0288$, $R_w = 0.0284$ for 2089 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta \leq 50^\circ$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

X-Ray analysis of **1** shows that in this complex each *trans*- UO_2^{2+} unit has bonded to it two bidentate nitrates and the oxygen atoms of two ebpyrr ligands in an eight-coordinate hexagonal bipyramidal coordination geometry. The *cis*-coordinated ebpyrr ligands serve to bridge adjacent $UO_2(NO_3)_2$ units so as to form a helical chain polymer that spirals along the crystallographic c direction (Fig. 1).[§] Each crystal contains chains of one helicity only. (However, as the compound crystallises in an enantiomorphous space group, there is an equal probability of selecting a crystal of either helicity). The hydrophobic bridging ethylene groups lie on the interior of the helix, whilst the hydrophilic nitrates dominate the exterior (Fig. 2). Adjacent helices are interleaved and the only notable inter-helix contact is between the oxygen atoms of neighbouring UO_2 units, which approach to within 2.99 Å.

X-Ray analysis of **2** reveals that in this complex one nitrate group has been replaced in the equatorial plane around the uranium atom by a peroxo-group (Fig. 3). Furthermore in **2** the ebpyrr ligands are now bonded in *trans*-positions, in contrast to their *cis*-arrangement in **1**. This results in the formation of a discrete 18-membered ring consisting of two U centres and two ebpyrr ligands. The formation of this ring system, as opposed to the helical array in **1**, may in part be attributed to the change from the *gauche*-N-CH₂-CH₂-N-unit in **1** to an *anti*-geometry in **2**.

The two U atoms in **2** are further linked by the peroxo-ligand which forms a μ - η^2 , η^2 -peroxo-bridge. The $U(\mu-O_2)U$ unit is folded by 138.5° about the O-O axis (Fig. 4). This results in a close approach (3.11 Å) of two of the axial oxygen atoms on adjacent U atoms. A similar folded peroxo-bridge geometry has been reported² in the complex $[(UO_2)_2(NO_3)_2O_2(\text{dmf})_4]$ (dmf = *N,N*-dimethylformamide) **3** in which the fold angle is somewhat larger (145°) and the uranyl group $O \cdots O$ separation consequently longer (3.26 Å).

The peroxo O-O distance [1.469(13) Å] is in the range expected for a peroxo ligand³ {*cf.* 1.483(7) Å in **3**;² 1.49(3) Å

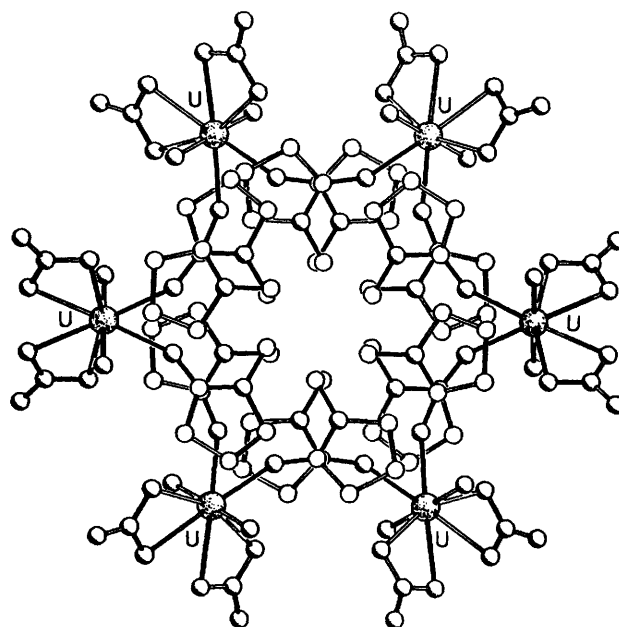


Fig. 2 A parallel projection looking along the crystallographic 6_1 screw axis in **1**, showing how the hydrophobic -CH₂-CH₂- linkages line the interior and the hydrophilic NO₃ groups occupy the exterior of the helix

[§] There are two crystallographic two-fold axes, one lying in the equatorial plane of the uranium atom, and bisecting the O(2)-U-O(2b) angle, and another passing through the centre of the C(6)-C(6a) bond of the ebpyrr ligand.

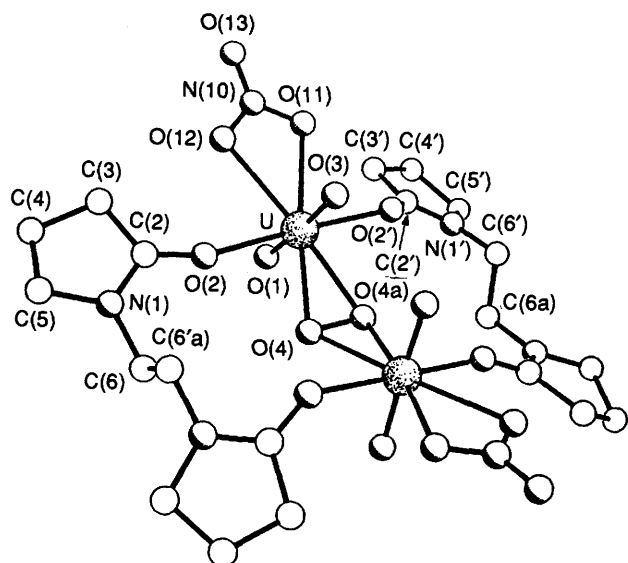


Fig. 3 The peroxo-bridged 18-membered ring present in **2**, showing the *anti* geometry present in the linking ebypr ligands

in the $[\text{Cl}_3\text{O}_2\text{U}(\mu\text{-O}_2)\text{UO}_2\text{Cl}_3]^{4-}$ ion⁴ but it is noticeably longer than the values (1.41–1.43 Å) found for some dinuclear Cu^{II} peroxo bridged complexes,⁵ of interest as oxyhaemocyanin and oxytyrosinase models. The IR spectrum of **2** shows a medium–weak band at 774 cm^{-1} which is not present in the spectrum of **1** and we tentatively assign this to $\nu(\text{O-O})$.

In **2** the molecules pack to form sheets whose planes lie perpendicular to the crystallographic *b* direction. Adjacent sheets are offset with respect to each other and the only significant inter-sheet contact (3.22 Å) is between one of the uranyl oxygens, O(1), in one sheet and a nitrate oxygen atom, O(13), in another.

Although the ring structure adopted by the $\text{U}_2(\text{ebpyrr})_2$ units in **2** clearly facilitates the formation of the $\mu\text{-}\eta^2, \eta^2$ -peroxo-bridge on geometric grounds, the mechanism of formation is unclear. With ligands related to **1**, we have observed⁶ individual large rings containing pairs of, *e.g.*, Co or Zn atoms. It is therefore tempting to postulate that similar

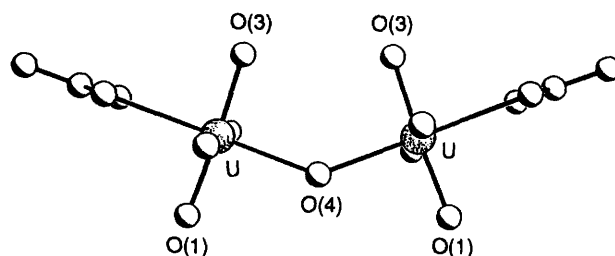


Fig. 4 The folding of the $\text{U}(\mu\text{-O}_2)\text{U}$ unit and associated close approach of the symmetrically related pairs of axial oxygen atoms in **2** ($\text{U}\cdots\text{U} = 4.14\text{ Å}$)

rings, or short chain length precursors to such rings, are produced in the reaction solutions which produce crystals of **1**. Any $\text{UO}_2^{2+} \rightarrow \text{UO}_2^+$ reduction (as proposed by Charpin *et al.*² as the initial step in the formation of **3**) would facilitate loss of a coordinated nitrate group. That in turn would permit binding of dioxygen between pairs of U atoms and subsequent electron transfer to produce the observed complex.

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