Binding of the uranyl moiety by an Amavadin-style complex; synthesis and characterisation of $[\{UO_2(H_2O)_3\}\{\Delta\text{-}V(hida)_2\}\cdot 2H_2O]_n$

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$[\Delta\text{-}V(hida)_2]^{2-}$ (H_3hida = *N*-hydroxyiminodiacetic acid) and UO_2^{2+} form the solid $[\{UO_2(H_2O)_3\}\{\Delta\text{-}V(hida)_2\}\cdot 2H_2O]_n$ which is comprised of left-handed helical arrays, linked by H-bonding networks, in which the V^{IV} is eight-coordinate and the U^{VI} seven-coordinate.

Recent studies in these laboratories have established that 2,2′-(*N*-hydroxyimino)dicarboxylic acid proligands form a range of distinctive eight-coordinate complexes with early d-transition metal centres such as Ti^{IV}, V^{IV}, V^{V}, Nb^{V}, Ta^{V} and Mo^{V}.[1–5] This work was initiated by the discovery of Amavadin,[6] originally isolated from mushrooms of the genus *Amanita* and constituted as a 1 : 2 complex of V^{IV} with (*S*,*S*)-2,2′-(*N*-hydroxyimino)dipropionic acid (H_3hidpa).[7] Amavadin possesses a novel eight-coordinate geometry, with each hidpa^{3-} ligand bonding *via* an η^2-NO group and two unidentate carboxylate groups. This coordination geometry leads to chirality at the vanadium and the isolated natural product Amavadin contains an approximately equimolar mixture of the Δ- and Λ-isomers of $[V\{(S,S)\text{-hidpa}\}_2]^{2-}$.[1,8] Amavadin-style anions form extended structures with cations such as Ca^{2+} *via* bridging caboxylate groups.[4,5] We have explored the possibility of extending this ‘cation-trapping’ by Amavadin-style complexes to other metals and, herein, we report the synthesis and characterisation of $[\{UO_2(H_2O)_3\}\{\Delta\text{-}V(hida)_2\}\cdot 2H_2O]_n$ **I** [H_3hida = 2,2′-*N*-hydroxyimino(diacetic acid)].

I was formed by the addition of $UO_2(O_2CMe)_2\cdot 2H_2O$ to an aqueous solution of $H_2[\Delta,\Lambda\text{-}V(hida)_2]$[9] and obtained as brown prismatic crystals.† The V^{IV} centres (Fig. 1) consist exclusively of $[\Delta\text{-}V(hida)_2]^{2-}$ moieties, each with the eight-coordinate geometry characteristic of Amavadin[1] with two mutually *trans* η^2-NO groups and four unidentate carboxylate groups. The dimensions of the V^{IV} centres are very similar to those obtained previously for this anion and its close relatives.[1,4,8,12] A striking aspect of **I** is that only the Δ-form of $[V(hida)_2]^{2-}$ was observed in the crystal subjected to X-ray crystallographic analysis; no vanadium-containing material remained in solution after crystallisation and we presume that a racemic mixture of ‘left’ and ‘right’ handed crystals was produced and one hand was arbitrarily selected for study.

In **I**, each U^{VI} centre is seven-coordinate (Fig. 1) with a pentagonal bipyramidal coordination geometry; the *trans* oxo-groups [O(11) and O(15)] are the axial ligands and the equatorial plane is comprised of three H_2O molecules [O(12), O(13) and O(14)] and two carboxylate oxygens from different $[\Delta\text{-}V(hida)_2]^{2-}$ centres [O(2*) and O(9)]. An approximate twofold axis of symmetry is located along the U–O(13) bond; O(11)–U–O(15) is effectively linear [177.1(6)°] and perpendicular (90.0°) to the least-squares plane of U and the five equatorial oxygen atoms; O(9) and O(14) sit above (0.05 and 0.06 Å, respectively) and U, O(12), O(13) and O(2*) sit below (−0.01, −0.02, −0.02, −0.06 Å, respectively) the least-squares plane. This coordination geometry is well known for seven-coordinate U^{VI} compounds[13] and may be directly compared with that of $[UO_2(orotato)_2(H_2O)_3]$‡,[14] which involves two orotato ligands in *cis* positions in the equatorial plane each coordinated *via* a unidentate carboxylate group. The U–O distances of **I** are similar to those in $[UO_2(orotato)_2(H_2O)_3]$ and related U^{VI} complexes.[13,14]

The unit cell of **I** is comprised of four identical and parallel left-handed helical chains centred on cell edges, each contributing its atoms to four unit cells; each turn of the helix is composed of six V^{IV} and six U^{VI} centres (Fig. 2). There are four solvent fragments in the lattice beyond the helical chains which, in the crystallographic refinement, were assumed to be H_2O molecules at 0.5 occupancy each. There is a network of short interhelix contacts, consistent with extensive H-bonding throughout the lattice, in particular: the uranyl *trans* oxo-groups H-bond to protons on different anions in neighbouring chains, O(15)···H(6b) and O(11)···H(3b) (2.4, 2.4 Å, respectively); and the water molecule O(13) coordinated to the U^{VI} has close contacts with carboxylates on different helical chains, O(13)···O(4) and O(13)···O(7) (2.5, 2.5 Å, respectively); these carboxylates also have close contacts with hydrogens on neighbouring anions, O(4)···H(7b) and O(7)···H(2b) (2.6, 2.7 Å, respectively); uncoordinated water molecules also have close contacts with water molecules coordinated to U^{VI}, O(12)···O(17) and O(14)···O(16) (2.7, 2.7 Å, respectively).

The IR spectrum of **I** contains ν(C=O) bands at 1637, 1617, and 1587 cm^{-1} and the different frequencies are consistent with the different roles of the carboxylate groups in bridging to the U^{VI} centres (Fig. 1). The ν(O=U=O) asymmetric stretching

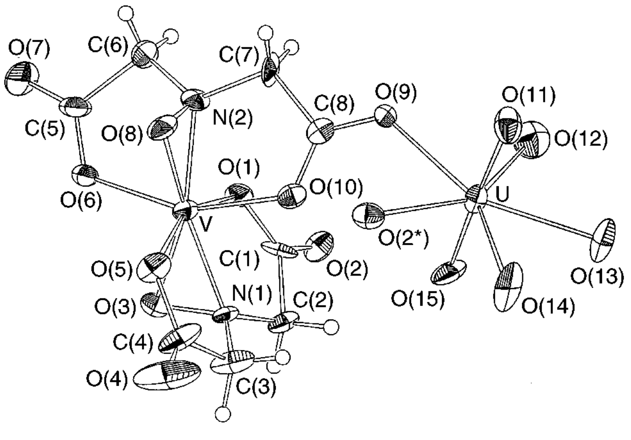

Fig. 1 V^{IV} and U^{VI} centres of **I**: selected bond lengths (Å) and interbond angles (°) U–O(2*) 2.36(1), U–O(9) 2.35(1), U–O(11) 1.71(2), U–O(12) 2.42(2), U–O(13) 2.39(1), U–O(14) 2.47(1), U–O(15) 1.69(2), V–O(1) 2.06(1), V–O(3) 1.95(2), V–O(5) 2.08(1), V–O(6) 2.07(1), V–O(8) 1.89(2), V–O(10) 2.05(2), V–N(1) 2.01(2), V–N(2) 1.95(2); O(2*)–U–O(9) 76.0(4), O(2*)–U–O(11) 92.1(7), O(2*)–U–O(14) 71.1(5), O(2*)–U–O(15) 90.3(7), O(9)–U–O(11) 88.9(7), O(9)–U–O(12) 72.2(5), O(9)–U–O(15) 93.1(6), O(11)–U–O(12) 90.1(8), O(11)–U–O(13) 89.8(7), O(11)–U–O(14) 88.5(8), O(12)–U–O(13) 69.0(6), O(12)–U–O(15) 88.6(8), O(13)–U–O(14) 71.9(6), O(13)–U–O(15) 87.3(8), O(14)–U–O(15) 90.9(8). The dihedral angle between {VNO} planes is 85.34°. * Indicates an atom derived by symmetry.

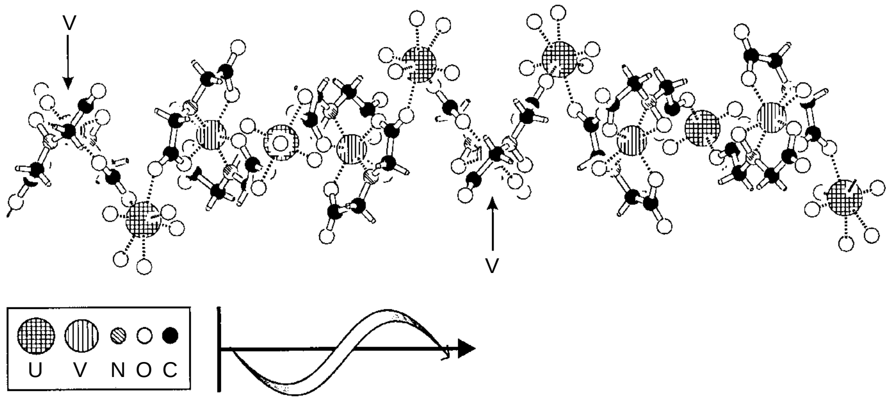

Fig. 2 Representation of a left-hand helical chain of **I**

frequency is manifest in the IR spectrum by a sharp absorption at 930 cm^{-1}.

Solid state reflectance UV–VIS data reveal absorptions due to the uranyl moiety, composed of progressions (average separation 625 cm^{-1}) arising from UO_2^{2+} symmetric stretching centred at 22 700 cm^{-1}; as well as d–d bands due to the V^{IV} centre at 12 100, 14 400 and 18 800 cm^{-1} and charge transfer transitions at $> 26\,300$ cm^{-1}.

The EPR spectrum of a polycrystalline powder of **I** at Q-band frequency at room temp. comprises a single broad (ΔB_{p-p} 235 G) line with a very asymmetric derivative shape indicative of axial symmetry with $g_{\parallel} = 1.932$, $g_{\perp} = 1.979$. This is consistent with a magnetically concentrated sample arising from the relatively short inter- and intra-helix V–V distances.

The 'trapping' of metal cations by Amavadin-style anions may allow the selective binding of cations, either to immobilise them or for ion exchange.[15] In this context it is of interest to note that competition experiments have demonstrated the preferential precipitation of UO_2^{2+} by the diffusion of MeOH into an aqueous solution of $H_2[V(hida)_2]$ containing equimolar amounts of UO_2^{2+} and Ca^{2+}.

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Notes and References

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† [VO(pentane-2,4-dionate)$_2$] (0.13 g, 0.5 mmol) was added to a stirred solution of H_3hida (0.15 g, 1 mmol) in H_2O (5 cm^3) at room temp.;[9] after dissolution, $UO_2(O_2CMe)_2\cdot 2H_2O$ (0.21 g, 0.5 mmol) was added and the solution stirred for *ca.* 3 h. Crystals of **I** suitable for X-ray diffraction were grown by slow vapour diffusion of MeOH into the reaction solution at 275 K. Analysis. Found: C, 14.2; H, 2.5; N, 4.0; U, 33.1 V, 7.4. Calc. for $C_8H_{18}N_2O_{17}UV$: C, 13.7; H, 2.6; N, 4.0; U, 33.9; V, 7.2%. *X-Ray crystal data for* **I**: $C_8H_{20}N_2O_{17}UV$, $M = 705.22$, hexagonal, space group $P6_5$ (no. 170), $a = 9.534(2)$, $c = 38.300(3)$ Å, $U = 3014(1)$ Å^3 (by least squares refinement on diffractometer angles of 25 automatically centred reflections), $\lambda = 0.710\,69$ Å, $Z = 6$, $F(000) = 1998$, $D_c = 2.330$ g cm^{-3}, $\mu = 85.99$ cm^{-1}, brown prismatic crystal of dimensions $0.20 \times 0.22 \times 0.25$ mm. Data were collected at 296 K using a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator. A total of 3988 reflections were measured in the ω scan mode to a $2\theta_{max}$ of 50.1°, which gave 1849 independent reflections ($R_{int} = 0.035$). An empirical absorption correction was applied, based on the azimuthal scans of several reflections (transmission factors: 0.6784–1.00). A decay correction was also applied (1.39% decline). 1587 reflections had $I > 1.50\sigma(I)$. The structure was solved by direct methods[10] and expanded using Fourier techniques.[11] The non-hydrogen atoms were refined anisotropically except for O(12) and the disordered water molecules O(16)–O(19), which were refined isotropically. Hydrogen atoms were included but not refined. Refinement of the 255 variables converged with $R = 0.044$, $R_w = 0.037$. Max., min. peaks in the final difference map 0.96, -0.93 e$^-$ Å^{-3}.

Careful consideration was given to the space group symmetry. There were four possible options, $P6_1$ and $P6_122$ and the alternative hands $P6_5$ and $P6_522$. The absolute configuration was determined by carrying out refinements in each space group using all of the observed data, including equivalent reflections. The detailed arguments which led to the selection of $P6_5$ as the correct space group are available as supplementary material from the corresponding author. CCDC 182/752.

‡ $[UO_2(orotato)_2(H_2O)_3]$ = dioxobis(1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidinecarboxylato)triaquauranium(vi).

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