The Molybdenum Analogue of Amavadin

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$[Mo^V(hidpa)_2]^-$ [$hidpa^{3-}$ = (oxyimino)dipropionate(3−)] has been synthesised and shown to possess the novel, octacoordinated structure identified for Amavadin, the form in which vanadium(IV) is bound in *Amanita muscaria* mushrooms; $[Mo^V(hidpa)_2]^-$ is capable of *both* a one-electron reduction and a one-electron oxidation.

Mushrooms of the genus *Amanita* accumulate vanadium to a concentration of ≤400 mg kg^{-1} (dry weight)[1] in the form of the discrete moiety Amavadin.[2] This is a 1:2 complex of V^{IV} with *S*,*S*-2,2′-(oxyimino)dipropionate(3−), $^-ON\{CH(Me)CO_2^-\}_2$ ($hidpa^{3-}$).[3,4] The presence of V^{IV} is clearly indicated by EPR spectroscopy[2,3,5–8] and the centre may be reversibly oxidized to the V^V level;[9] thus, this species belongs to the group of transition metal centres in biology which exhibit one-electron reversible redox behaviour. Recent studies[10] have established that Amavadin comprises a novel octacoordinated complex, with each $hidpa^{3-}$ ligand coordinated *via* the η^2-*N*,*O* group and two unidentate carboxylate groups. This coordination environment leads to chirality at the vanadium, and Amavadin, as isolated, consists of an approximately equal mixture of the Δ- and Λ- forms of $[V(S,S\text{-hidpa})_2]^{2-}$. A comparison of the electronic structure of Amavadin with both related complexes and VO^{2+} complexes, suggests a chemical[11] and an electronic[12] equivalence between the bonding of two mutually *trans*-η^2-*N*,*O* groups and one oxo group.

The unusual geometry and chemical behaviour of Amavadin has generated curiosity as to whether it is possible to extend this chemistry to other metals. Therefore, we have investigated the reactivity of H_3hidpa towards other oxo-metal centres, especially those found in biological systems. Herein we report the synthesis† and characterisation of the first example of a chemical analogue of Amavadin, $[Mo(hidpa)_2]^-$, a 1:2 complex of Mo^V with $hidpa^{3-}$. $[PPh_4][Mo(hidpa)_2]$ crystallises‡ in the centrosymmetric space group $P\bar{1}$. The anion, shown in Fig. 1, has the same overall structure[10,15] as $[V(hidpa)_2]^-$, $[V(hida)_2]^-$ and $[V(hida)_2]^{2-}$ ($hida^{3-}$ = $^-ON\{CH_2CO_2^-\}_2$). Thus, the molybdenum is coordinated to two mutually *trans* η^2-*N*,*O* groups and four unidentate carboxylate groups. The Mo–O and Mo–N bonds are each slightly longer (range 0.11–0.03 Å; av. 0. 06 Å) than their counterparts in Δ-$[V(S,S\text{-hidpa})_2]^-$.[10] The η^2-*N*,*O* groups subtend angles of 39.1(3) and 40.1(3)° at molybdenum which compare with the range 39.9–41.2° observed for the related vanadium systems.[10,15] The planes of the two {MoNO} groups are approximately perpendicular (86.2°) and each is effectively perpendicular (89.4; 88.6°) to the least-squares plane of the molybdenum and the four coordinated carboxylate oxygen atoms. These oxygen atoms are significantly displaced from this least-squares plane; O(1) and O(5) sit below (−0.43 and −0.34 Å, respectively) and O(6) and O(10) sit above (0.32 and 0.43 Å, respectively) the plane, which does contain the molybdenum. For the convenience of discussing the electronic structure of this type of complex,[11] the axis system is chosen so that the *x*- and *y*-axes lie in the least-squares plane and are directed towards the carboxylato-oxygen atoms and the *z*-axis approximately bisects the O–Mo–N angles subtended by the two oxyimino-groups at the metal. The complex shown in Fig. 1 involves specific chiralities at the molybdenum and at the ligand β-carbons, as Δ-$[Mo(R,R\text{-hidpa})(R,S\text{-hidpa})]^-$. The unit cell also contains the isomer related by the centre of symmetry, *i.e.* Δ-$[Mo(S,S\text{-hidpa})(S,R\text{-hidpa})]^-$.

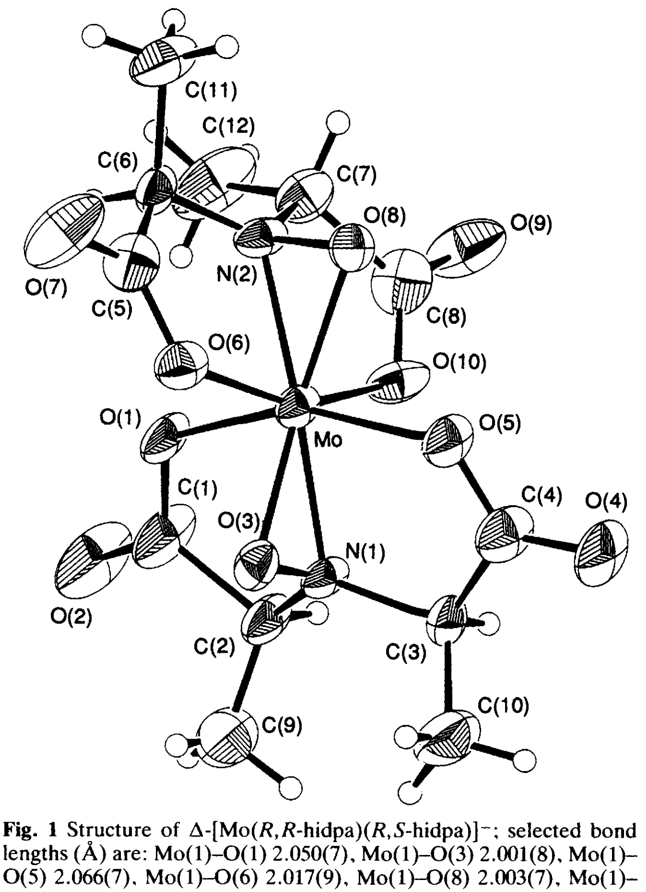

Fig. 1 Structure of Δ-$[Mo(R,R\text{-hidpa})(R,S\text{-hidpa})]^-$; selected bond lengths (Å) are: Mo(1)–O(1) 2.050(7), Mo(1)–O(3) 2.001(8), Mo(1)–O(5) 2.066(7), Mo(1)–O(6) 2.017(9), Mo(1)–O(8) 2.003(7), Mo(1)–O(10) 1.99(1), Mo(1)–N(1) 2.055(8), Mo(1)–N(2) 2.054(9)

The X-band EPR spectrum of $[PPh_4][Mo(hidpa)_2]$ in CH_2Cl_2–toluene at ambient temperature consists of a central resonance, g_{iso} = 1.945, symmetrically flanked by 6 hyperfine resonances, A_{iso} = 44.5 × 10^{-4} cm^{-1}. The frozen solution spectrum appears rhombic and the parameters g_1 = 1.894, A_1 = 76.0 × 10^{-4} cm^{-1}; g_2 = 1.967, A_2 = 32.1 × 10^{-4} cm^{-1}, g_3 = 1.974, A_3 = 27.6 × 10^{-4} cm^{-1} successfully simulate the profile. By analogy with $[V(hidpa)_2]^{2-}$ [11] we consider that the unpaired electron in $[Mo(hidpa)_2]^-$ is located in the d_{xy} orbital. $[PPh_4][Mo(hidpa)_2]$ is a brown–purple colour and the electronic absorption spectrum in MeCN includes a broad band centred at *ca.* 550 nm (ε = 18 mol l^{-1} cm^{-1}) and a band at

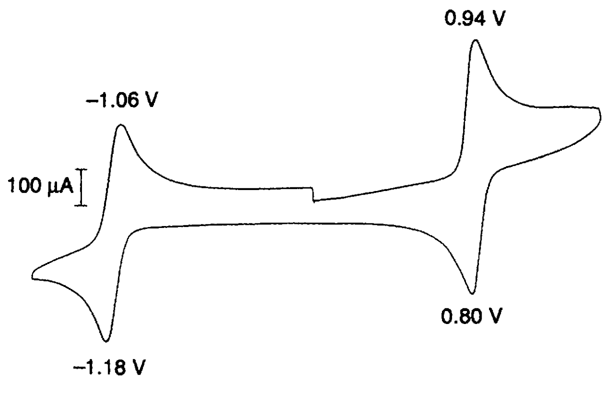

Fig. 2 Cyclic voltammogram recorded at a glassy carbon electrode (*vs.* SCE) for $[PPh_4][Mo(hidpa)_2]$ (0.001 mol dm^{-1}) CH_2Cl_2 containing $[NBu_4^n][BF_4]$ (0.2 mol dm^{-1})

385 nm (ε = 89 mol l^{-1} cm^{-1}) on a sharply rising background. By analogy with the electronic structure proposed for the vanadium systems,[11] these transitions are assigned as $d_{xy} \rightarrow d_{xz,yz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$, respectively.

Cyclic voltammetric studies (Fig. 2) show that [PPh$_4$][Mo(hidpa)$_2$] in CH_2Cl_2 is capable of both a one-electron reversible oxidation at $E_{\frac{1}{2}}$ = +0.87 V and a one-electron reversible reduction at $E_{\frac{1}{2}}$ = −1.12 V (*vs.* SCE), using ferrocene as an internal calibrant. These processes are considered to be metal-based by comparison with the corresponding vanadium systems. However, the redox behaviour of [Mo(hidpa)$_2$]$^-$ is more versatile than that observed for [V(hidpa)$_2$]$^{2-}$ complexes, since only a V^{V}/V^{IV} couple has been identified under similar experimental conditions.[9] The similarity of the profile of the electronic absorption spectrum of [Mo(hidpa)$_2$]$^-$ to those of oxomolybdenum(v) complexes[16] reinforces the electronic equivalence suggested[11] for one oxo-group and two mutually *trans* η^2-*N,O* groups. This is paralleled by the redox properties of [Mo(hidpa)$_2$]$^-$ as compared to [V(hidpa)$_2$]$^{2-}$; the behaviour of the former corresponds to the sequence[17] $Mo^{IV}O^{2+} \leftrightarrow Mo^{V}O^{3+} \leftrightarrow Mo^{VI}O^{4+}$ and that of the latter to the couple $V^{IV}O^{2+} \leftrightarrow V^{V}O^{3+}$.

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Footnotes

† [PPh$_4$][Mo(hidpa)$_2$] was prepared by adding [MoO$_2$(acac)$_2$][13] to a stirred, aqueous solution of H$_3$hidpa—the proligand having been prepared from a racemic mixture of ±-2-bromopropionic acid[14]—followed by phase transfer into CH_2Cl_2 containing [PPh$_4$]Br. The brown-purple product was precipitated by the addition of Et_2O and diffraction quality crystals were obtained by dissolution in CH_2Cl_2, into which toluene was diffused slowly.

‡ [PPh$_4$]$_2$$\Delta$-[Mo(*R,R*-hidpa)(*R,S*-hidpa)]Δ-[Mo(*S,S*-hidpa)(*S,R*-hidpa)] crystallises in the $P\bar{1}$ space group with a = 11.14(1), b = 16.87(1), c = 10.054(5) Å, α = 95.18(6), β = 94.53(6), γ = 106.40(7)°, V = 1795(2) Å^3, Z = 2; F(000) = 806; D_c = 1.450 g cm^{-3}; μ = 4.56 cm^{-1}; Mo-Kα radiation; $2\theta_{max}$ = 50.0°; 6690 reflections measured, 3059 observed ($I > 3\sigma I$); number of parameters 451; R = 0.070, R_w = 0.080. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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