FULL PAPER

New molybdenum(v) analogues of Amavadin and their redox properties

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Reactions of $[MoO_2(acetylacetonate)_2]$ with the proligands (*N*-hydroxyimino)diacetic acid (H₃hidpa), *R*,*R*-2,2'-(*N*-hydroxyimino)dipropionic acid (*R*,*R*-H₃hidpa) or *R*,*S*-2,2'-(*N*-hydroxyimino)dibutyric acid (*R*,*S*-H₃hidba) yielded the compounds $[PPh_4][\Delta,\Lambda$ -Mo(hida)_2]·CH₂Cl₂ **1**, $[H_5O_2][\Delta$ -Mo(*R*,*R*-hidpa)_2] **2**, $[PPh_4][Mo(R,S-hidba)_2]$ · $2H_2O$ **3a** and Na[Δ,Λ -Mo(*R*,*S*-hidba)_2]·'/⁴Pr₂O **3b**, respectively. Reactions of H₃hida with a methanolic solution of $[PPh_4][MoOCl_4(H_2O)]$ in the presence of NaOH (*ca*. pH 8) provided an alternative synthesis for **1**. The complex of **1** when transferred into CH₂Cl₂ using $[PPh_4]$ Br yielded brown block-like crystals from a CH₂Cl₂–EtOH solution, however, **2** and **3b** were crystallised from H₂O and MeCN solutions with $[H_5O_2]^+$ and $[Na]^+$ counter cations, respectively. X-Ray crystallography confirmed the same distinctive eight-co-ordinate geometry of the complex anions of **1**, **2** and **3b** as identified for Amavadin, the form in which vanadium(IV) is bound in *Amanita muscaria* mushrooms. EPR and UV/vis spectra recorded for **1**, **2** and **3a** are consistent with the presence of molybdenum(v). Cyclic voltammetric studies using a glassy carbon working electrode in CH₂Cl₂ for **1** exhibited a reversible Mo^{VI}/Mo^V and a quasi-reversible Mo^V/Mo^{IV} redox couple at $E_{1/2} = +0.96$ and -0.99 V (*vs.* a saturated calomel electrode), respectively. Complex **3a** also displayed a reversible Mo^{VI}/Mo^V redox couple at $E_{1/2} = +0.77$ V, whereas the Mo^V/Mo^{IV} couple was irreversible ($E_{pc} = -1.28$ V). Additional electrochemical studies with **2** recorded a reversible Mo^{VI}/Mo^V redox couple in Me₂SO ($E_{1/2} = +0.77$ V), however in H₂O this one-electron oxidation process is irreversible.

Introduction

Mushrooms of the genus Amanita accumulate vanadium to concentrations of up to 400 mg kg⁻¹ (dry weight)¹ in the form of the discrete moiety Amavadin,² a 1 : 2 complex of vanadium(IV) with the proligand S,S-N-hydroxyiminodipropionic acid $(S,S-H_3hidpa = HON\{CH(CH_3)CO_2H\}_2)$.³⁻⁵ The presence of V^{IV} is clearly indicated by EPR spectroscopy⁶ and the metal centre can be reversibly oxidised to the V^V level.⁷ Thus this species belongs to the group of transition metal centres in biology which exhibit reversible, one-electron, redox behaviour. This redox behaviour may account for the biological role of Amavadin and, in solution, has been shown to mediate the oxidation of glutathione and other biologically active thiols.^{8,9} Recent studies^{5,10,11} into the chemical nature of Amavadin have established a novel eight-co-ordinate geometry, with each S,S-H₃hidpa proligand co-ordinated via an η^2 -NO group and two unidentate carboxylate groups. Complementary work 10,12,13 has included the analogues from N-hydroxyiminodiacetic acid $(H_3hida = HON\{CH_2CO_2H\}_2)$ which provide further examples of this distinctive eight-co-ordinate structure. This co-ordination environment leads to chirality at the vanadium (Scheme 1) and the isolated natural product Amavadin consists of an approximately equimolar mixture of the Δ - and Λ -helical forms of $[V(S,S-hidpa)_2]^{2-.10,11}$ These complexes are assigned idealised C2 point symmetry in solution, where the two-fold axis bisects angles between the normals to the {VNO} plane from each ligand projected



through the metal atom. The special co-ordination geometry and chemical behaviour of Amavadin has generated curiosity as to whether it is possible to extend this chemistry to Therefore, studies of the reactivity other metals. H₃hidpa towards other metal centres, especially those found in biological systems, were initiated. The synthesis and characterisation of $[PPh_4][\Delta-Mo(R,R-hidpa)(R,S-hidpa)]$ and its enantiomer,14 that involve molybdenum(v) bound to two mutually trans n²-NO groups and four unidentate carboxylates, was the first example of a chemical analogue of Amavadin. This complex is capable of both a one-electron reversible oxidation and a one-electron reversible reduction in CH₂Cl₂. Other developments, notably studies of $[M(hidca)_2]^{-/2-}$ (H₃hidca = *N*-hydroxyiminodicarboxylic acid, $HON\{CH(R)CO_2H\}_2$, for R = alkyl) have been reported,¹⁵ and the chemistry described herein has led to several new molybdenum complexes related to Amavadin.

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Reagents and apparatus

All reagent and solvents were obtained from normal commercial sources and were used without further purification unless otherwise stated. Tetrahydrofuran (thf) and Et₂O were distilled from sodium; CH₂Cl₂ and MeCN were distilled from CaH₂, and all solvents were stored under dinitrogen. The proligands H_3 hida and $R, R-H_3$ hidpa were synthesised using a modification of the method 16 described by Felcman et al., 17 and purification was carried out using the procedure outlined by Koch et al.¹⁸ R,S-H₃hidba (R,S-N-hydroxyiminodibutyric acid = HON{ $CH(C_2H_5)CO_2H_2$) was synthesised as described by Smith *et al.*¹⁵ [MoO₂(acetylacetonate)₂] was synthesised as described by Jones,¹⁹ by treatment of an aqueous solution of Na₂[MoO₄] with HCl (ca. pH 1) and acetylacetone to produce a yellow precipitate. [PPh4][MoOCl4(H2O)] was prepared as a green crystalline product from a solution of [MoCl₅] in conc. HCl in the presence of [PPh₄]Cl.²⁰ Chemical analyses were performed by The University of Manchester, Microanalytical Laboratory. IR spectra were recorded on a Perkin-Elmer 1710 FT spectrometer. Electronic absorption spectra were recorded on a Varian Cary 1E UV/vis spectrophotometer. Mass spectra were recorded using a KRATOS concept 1S spectrometer (matrix NBA). X-Band (ca. 9.5 GHz) EPR spectra were recorded on a Bruker ESP300E spectrometer.

Electrochemical measurements were made with a PAR model 175 waveform generator, a model 173 potentiostat, and a PAR electrochemistry cell with a three-electrode configuration consisting of a glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire secondary electrode. Data were recorded on an Advance Bryans Series 6000 XY/t recorder. The cyclic voltammograms were recorded for solutions of compound (ca. 1 mmol dm^{-3}) with [NBuⁿ₄]-[BF₄] (ca. 0.2 mol dm⁻³) as supporting electrolyte in nonaqueous media, prepared from Na[BF₄] and [NBuⁿ₄][HSO₃] and recrystallised from toluene.²¹ KCl (ca. 0.2 mol dm⁻³) was used as supporting electrolyte for cyclic voltammograms recorded in H₂O. Controlled potential electrolysis (CPE) experiments were carried out in a two-compartment cell separated by Vycor porous glass. The working electrode consisted of a cube of reticulated vitreous carbon, purchased from The Electrosynthesis Co, Inc., Lancaster, NY 14086, and the secondary electrode was platinum mesh. All solutions were deoxygenated by bubbling dinitrogen through them for several minutes prior to use and all voltammograms were recorded with solutions under a dinitrogen atmosphere at 293 K. An optically transparent thin layer electrode (OTTLE) was supported in a cell and poly(tetrafluoroethylene) block from the design developed by Heath et al.²² All electrochemical potentials were measured relative to SCE and were corrected for liquid-junction potentials in non-aqueous media via the use of the ferrocenium-ferrocene couple as an internal redox standard $([(Cp)_2Fe]^+/[(Cp)_2Fe]; \Delta E = 65 \text{ mV}, i_{pa}: i_{pc} = 0.96).^{23}$

Syntheses

[PPh₄][\Lambda, A-Mo(hida)₂]·CH₂Cl₂ 1. *Method 1.* **[MoO₂(acetylacetonate)₂] (326 mg, 1.00 mmol) was added to a solution of H₃hida (315 mg, 2.10 mmol) in H₂O (10 cm³). The reaction mixture was stirred (***ca.* **3 h) at 323 K, whereupon a dark brown–purple solution formed. After cooling (to** *ca.* **293 K), a solution of [PPh₄]Br (419 mg, 1.00 mmol) in CH₂Cl₂ (10 cm³) was mixed with the aqueous phase and after rapid stirring (for** *ca.* **30 min) the dark brown–purple colour transferred into the CH₂Cl₂ layer. The CH₂Cl₂ phase was separated from the aqueous layer and dried over anhydrous CaCl₂ (for** *ca.* **1 h), filtered and then EtOH (10 cm³) was added. Brown–purple block-like crystals were obtained by slow evaporation (***ca.* **48 h) at 293 K from the resulting solution, and these were collected and dried** under vacuum. Yield, 380 mg, 47% (Found: C, 48.74; H, 3.78; N, 3.54; Mo, 11.65; P, 3.9%. Calc. for $C_{33}H_{30}N_2O_{10}Cl_2MOP$: C, 48.71; H, 3.72; N, 3.44; Mo, 12.04; P, 3.81%). IR (KBr, cm⁻¹): 1690 [ν (C=O)], 1353 [ν (C–O)], 1108 [ν (N–O)]. UV/Vis (MeCN): ν /cm⁻¹ (ϵ /mol⁻¹ dm³ cm⁻¹) 26455 (103) and 18181 (19). Mass spectrum (negative-ion FAB): m/z 390 = [Mo(hida)₂]⁻.

Method 2. [PPh₄][MoOCl₄(H₂O)] (61 mg, 1.00 mmol) was dissolved in acetone (15 cm³) and dinitrogen bubbled through the solution. H₃hida (315 mg, 2.10 mmol) was dissolved in MeOH (6 cm³) and the pH (as measured by Whatman paper 3 pH 1–11 colour indicator paper) adjusted to 8 with NaOH (5 mol dm⁻³). On addition of the H₃hida solution to that of [PPh₄][MoOCl₄(H₂O)] an instant colour change occurred and a brown precipitate formed. The reaction mixture was stirred (for *ca.* 10 min) and then the solvent removed under vacuum. The resulting residue was extracted into CH₂Cl₂ (10 cm³), dried over anhydrous CaCl₂ (for *ca.* 1 h) and crystals were obtained from this solution as described in Method 1. Yield, 350 mg, 43% (Found: C, 48.12; H, 3.66; N, 3.38%. Calc. for C₃₃H₃₀N₂-O₁₀Cl₂MoP: C, 48.71; H, 3.72; N, 3.44%).

 $[H_5O_2][\Delta-Mo(R,R-hidpa)_2]$ 2. $[MoO_2(acetylacetonate)_2]$ (326) mg, 1.00 mmol) was added to a solution of R,R-H₃hidpa (431 mg, 2.10 mmol) in H₂O (10 cm³). The reaction mixture was stirred (for ca. 3 h) at 323 K, whereupon a brown solution formed, which was allowed to cool (to ca. 293 K) and was filtered. This solution was concentrated by evaporation under vacuum (2 cm³) and cooled (to ca. 273 K) then added to cold (ca. 273 K) thf (20 cm³) and a brown precipitate formed that was collected and dried under vacuum. Brown block-like crystals suitable for X-ray diffraction were obtained by slow evaporation of an aqueous solution of the precipitate at 293 K. Yield, 240 mg, 52% (Found: C, 30.4; H, 4.27; N, 5.78; Mo, 21.67%. Calc. for $C_{12}H_{21}N_2O_{12}Mo$: C, 29.81; H, 4.38; N, 5.8; Mo, 20.27%). IR (KBr, cm⁻¹): 1650 [v(C=O)], 1366 [v(C-O)], 1121 [v(N–O)]. UV/Vis (H₂O): v/cm⁻¹ (ε/mol⁻¹ dm³ cm⁻¹) 26041 (61) and 18181 (15). Mass spectrum (negative-ion FAB): m/z $444 = [Mo(hidpa)_2]^{-}$.

[PPh₄][Mo(R,S-hidba)₂]·2H₂O 3a. [MoO₂(acetylacetonate)₂] (326 mg, 1.00 mmol) was added to a solution of R,S-H₃hidba (431 mg, 2.1 mmol) in MeOH (10 cm³) and the reaction mixture was stirred (for ca. 18 h) at 293 K, whereupon a brown solution formed. [PPh₄]Br (419 mg, 1.00 mmol) was added and the solution evaporated to dryness under vacuum. The resulting residue was extracted into thf (10 cm³) and filtered to remove any excess [PPh₄]Br. This solution was cooled (to 275 K) and added dropwise into cold (275 K) Et₂O (50 cm³) and produced a brown precipitate. The solid product was very hygroscopic and therefore was collected in a dinitrogen atmosphere, washed with Et₂O (10 cm³), dried under vacuum and stored under dinitrogen over silica-gel. Yield, 605 mg, 72% (Found: C, 53.75; H, 5.19; N, 3.17; Mo, 10.80; P, 3.28%. Calc. for C₄₀H₄₈N₂O₁₂MoP: C, 54.72; H, 5.51; N, 3.19; Mo, 11.16; P, 3.53%). IR (KBr, cm⁻¹): 1675 [v(C=O)], 1459 [v(C-O)], 1131 [v(N-O)]. UV/Vis (MeCN): v/cm⁻¹ (ε/mol⁻¹ dm³ cm⁻¹) 26595 (94) and 17730 (10). Mass spectrum (negative-ion FAB): m/z 502 = [Mo(hidba)₂]⁻.

Na[Δ , A-Mo(*R*, S-hidba)₂]· 1 · 1 Pr₂O 3b. [MoO₂(acetylacetonate)₂] (326 mg, 1.00 mmol) was added to a solution of *R*, S-H₃hidba (431 mg, 2.10 mmol) in MeOH (10 cm³), previously treated with NaOH (40 mg, 1.0 mmol). This reaction mixture was stirred (for *ca.* 18 h) at 293 K, whereupon a brown solution formed and was evaporated to dryness under reduced pressure. The resulting residue was extracted into MeCN (10 cm³) and red block-like crystals suitable for X-ray diffraction were obtained from this solution *via* the slow vapour diffusion technique using ¹Pr₂O at 273 K. Yield, 285 mg, 51% (Found: C, 34.81; H, 5.17; N, 5.07; Mo, 17.77; Na, 4.17%. Calc. for C₁₆H₂₄-N₂O₁₀MoNa·2H₂O: C, 34.35; H, 5.01; N, 5.00; Mo, 17.17; Na,

Empirical formula	$C_{33}H_{30}Cl_2MoN_2O_{10}P(1)$	$C_{12}H_{21}M_0N_2O_{12}$ (2)	C ₃₀ H ₅₅ N ₄ O ₂₀ 5Mo ₂ Na ₂ (3b)
Formula weight	812.43	481.25	547.32
Crystal colour, habit	Brown, block	Brown, block	Red, block
Crystal dimensions/mm	$0.20 \times 0.25 \times 0.35$	$0.8 \times 0.3 \times 0.3$	$0.17 \times 0.17 \times 0.25$
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
a/Å	7.96(1)	10.3610(10)	28.23(1)
b/Å	28.043(6)	13.9210(10)	30.29(1)
c/Å	15.47(1)	6.8470(10)	11.64(1)
BI°	91.54(8)	_	_
$V/Å^3$	3451(5)	987.6(2)	9956(17)
Space group	$P2_1/c$ (no. 14)	$P2_{1}2_{1}2$ (no. 18)	<i>Fddd</i> (no. 70)
Z	4	2	16
$D_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.564	1.618	1.460
μ/cm^{-1}	Cu-Ka, 55.76	Μο-Κα, 7.25	Cu-Ka, 49.33
Diffractometer	Rigaku AFC5R	Rigaku AFC7R	Rigaku AFC5R
λ/Å	1.54178	0.71073	1.54178
T/K	296 ± 1	293 ± 2	293 ± 1
Scan type	ω –2 θ	ω	ω –2 θ
$2\theta_{\rm max}/^{\circ}$	120.1	60	158.9
No. of reflections measured	Total: 5679	Total: 1674	Total:2857
	Unique: 5257	Unique: 1674	Unique: 2857
	$(R_{int} = 0.046)$	$(R_{int} = 0.0)$	*
Corrections	Lorentz-polarisation	Lorentz-polarisation	Lorentz-polarisation
	Absorption (DIFABS) ²⁴	*	Absorption (ψ -scans)
No. of observations	$3765 [\hat{I} > 3.00\sigma(I)]$	$1674 [I > 2.00\sigma(I)]$	$1583 [I > 2.00\sigma(I)]$
No. of variables	442	125	155
Residuals	$R = 0.098; R_w = 0.130$	$R = 0.0279; R_{w} = 0.0749 [I > 2\sigma(I)]$	$R = 0.064; R_w = 0.053$
		$R = 0.0297; R_{\rm w} = 0.0760$ (all data)	
Goodness of fit indicator	3.58	1.088	1.94

4.11%). UV/Vis (H₂O): ν/cm^{-1} (ϵ/mol^{-1} dm³ cm⁻¹) 24943 (60) and 17841 (13). Mass spectrum (negative-ion FAB): m/z 502 = [Mo(hidba)₂]⁻.

X-Ray crystallography

A summary of the crystallographic information obtained for 1, 2 and 3b is provided in Table 1. The structures were solved by direct methods using SIR^{24,25a} for 1 and SHELXS^{25a} for 2 and 3b. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations²⁶ in idealised positions (C–H = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than the equivalent *B* value of the atom to which they were bonded. For 1 and 3b all calculations were performed using the TEXSAN^{27a} crystallographic software package. For 2 the data were refined against F^2 using SHELXL93.^{27b}

CCDC reference numbers 168519–168521.

See http://www.rsc.org/suppdata/dt/b1/b102531g/ for crystallographic data in CIF or other electronic format.

Results and discussion

The values for the Mo analysis are reasonably close to the expected values, however the C, H, N, Na and P are closer and the spectral and crystallographic data are consistent with the formulae given.

Crystallography

After the initial investigation with vanadium^{5,10–13} and recent results with molybdenum,¹⁴ herein we report the structures of further examples of molybdenum(v) analogues of Amavadin. 1 forms brown block-like crystals in the space group $P2_1/c$ (no. 14) (Table 1). As expected, the complex anion exhibits the eightco-ordinate geometry found in Amavadin containing a 1 : 2 complex of molybdenum(v) with hida³⁻, bound by two mutually *trans* η^2 -NO groups and four unidentate carboxylates, see Fig. 1. The asymmetric unit contains half the complex anion and a [PPh₄]⁺ counter cation with a molecule of CH₂Cl₂. The anion was refined as the Δ -helical form at the molybdenum(v) centre. The space group has a centre of symmetry; therefore the equivalent Λ -isomer at the metal centre is generated in the unit



Fig. 1 ORTEP³⁹ representation of the structure of the anion present in 1.

cell. The Mo–O and Mo–N bond lengths are similar to those in [Δ -Mo(*R*,*R*-hidpa)(*R*,*S*-hidpa)]⁻¹⁴ (Table 2), and are each slightly longer (range 0.13–0.02 Å; av. 0.07 Å) than their counterparts in [V(hida)₂]^{-,10} The planes of the two {MoNO} groups are perpendicular (90.04°, as measured from N to O, see Scheme 1) and each is effectively perpendicular (88.92; 90.49°) to the least-squares plane of the molybdenum and the four-co-ordinated carboxylate oxygen atoms (the "equatorial" plane). These oxygen atoms are significantly displaced from this least-squares plane; O(1) and O(5) sit below (-0.42 and -0.38 Å, respectively) and O(6) and O(10) sit above (0.36 and 0.39 Å, respectively) the plane, which contains the molybdenum.

Initial reactions of $[PPh_4][MoOCl_4(H_2O)]$ with H_3 hidpa resulated in fragmentation of the proligand and yielded a product which contained a novel 2-(oxyimino)propionic acid moiety, $[PPh_4][MoO_2Cl_2(NOC(Me)CO_2H)]$.²⁸ X-Ray crystallography showed that the molybdenum(VI) was bound to two oxo groups, two chlorides, and the $[NOC(Me)CO_2H]$ fragment co-ordinated *via* the nitrogen and an oxygen atom in the $\{CO_2H\}$ group. However, when this reaction was repeated under basic conditions (see Experimental section), facile chloride abstraction was promoted and the eight-co-ordinate

Table 2 Comparison of selected bond lengths (Å) and angles (°) for 1, 2, 3b and $[PPh_4][Mo(R,R-hidpa)(R,S-hidpa)]^{14}$

	1	2 ^{<i>a,b</i>}	3b ^{<i>a</i>}	$[PPh_4][\Delta-Mo(R,R-hidpa)(R,S-hidpa)]$	
Mo(1)–O(1)	2.01(1)	2.064(2)	2.053(6)	2.050(7)	
Mo(1) - O(5)	2.04(1)	2.062(2)	2.039(6)	2.066(7)	
Mo(1)–O(6)	2.038(9)	2.064(2)	2.053(6)	2.017(9)	
Mo(1) - O(10)	2.074(9)	2.062(2)	2.039(6)	1.99(1)	
Mo(1) - O(3)	2.01(1)	2.002(2)	2.003(6)	2.001(8)	
Mo(1)–O(8)	2.00(1)	2.002(2)	2.003(6)	2.003(7)	
Mo(1) - N(1)	2.09(1)	2.070(2)	2.101(7)	2.055(8)	
Mo(1)–N(2)	2.09(1)	2.070(2)	2.101(7)	2.054(9)	
N(1)–O(3)	1.41(1)	1.394(3)	1.406(7)	1.36(1)	
N(2)–O(8)	1.46(1)	1.394(3)	1.406(7)	1.39(1)	
N(1)–Mo(1)–O(1)	40.0(4)	39.99(9)	40.0(2)	39.1(3)	
N(2)–Mo(1)–O(8)	41.9(4)	39.99(9)	40.0(2)	40.1(3)	

^{*a*} C_2 symmetry at the molybdenum centre, hence N(2), O(6), O(8), and O(10) are generated by symmetry. O(1,5,6,10) are carboxylate O atoms and O(3,8) are the η^2 -NO O atoms. ^{*b*} O(3) and O(5) renumbered for comparison.



Fig. 2 ORTEP representation of the structure of the anion present in **2**.

Amavadin-style complex was isolated, providing a rapid and alternative synthesis of **1**.

2 crystallised as brown blocks in the space group $P2_12_12_2$ (no. 18) (Table 1). The complex anion exhibits the eightco-ordinate geometry found in Amavadin, see Fig. 2. The asymmetric unit consists of half the complex anion with the Δ -form at the molybdenum(v) centre plus an oxygen atom (O6) around which three peaks were observed in the final difference map. These can be assigned to two full occupancy H atoms and one half occupancy H atom, lying close to the two-fold axis. The latter H-bonds to the symmetry equivalent water oxygen (O6A) generated by the two-fold axis generating an $[H_2O_5]^+$ unit with a slightly disordered central H atom. Thus, throughout the crystal structure there are complex anion units of $[\Delta$ -Mo(*R*,*R*-hipda)₂]⁻ linked by $[H_2O_5]^+$ units. The *R*,*R*-ligand can be used as a "lock" on the structure solutions since the chirality of the ligand is carried directly through to the complex.²⁹ The Mo atom sits on a crystallographic C_2 axis in the lattice, so the corresponding Mo-O and Mo-N bond lengths are identical within the two ligands and of a similar length to those in $[\Delta$ -Mo(*R*,*R*-hidpa)(*R*,*S*-hidpa)]⁻¹⁴ (Table 2), with each slightly longer (range 0.12-0.03 Å; av. 0.07 Å) than their conuterparts in $[\Delta - \tilde{V}(S, S-hidpa)_2]^{-10}$ The planes of the two {MoNO} groups are close to perpendicular (90.2°) and effectively perpendicular (91.2 and 91.2°) to the "equatorial" plane,



Fig. 3 ORTEP representation of the structure of the anion present in 3b.

with significant displacements for O(1) and O(3) (-0.43 and -0.36 Å, respectively).

3b crystallised in the space group *Fddd* (no. 70), with the eight-co-ordinate geometry of Amavadin (Fig. 3).⁵ The asymmetric unit contains half of the anion with the Mo atom located on a two-fold axis. This anion was refined as the Δ helical form at the molybdenum(v) centre and the Λ -form is generated by the symmetry of the unit cell. The ligand was refined in exclusively the R,S-chiral form. The asymmetric unit also contains half a sodium counter cation located on a twofold axis. Two "solvent atoms" were found disordered over two sites each, probably arising from ⁱPr₂O; it is not clear which atom is carbon and which is oxygen. As in 2, the Mo atom sits on a crystallographic C_2 axis in the lattice and corresponding Mo-O and Mo-N bond lengths are identical in the two ligands. The planes of the two {MoNO} groups are not mutually perpendicular (96.5°),³⁰ but are effectively perpendicular (88.9, 91.1°)³⁰ to the equatorial plane. These oxygen atoms are significantly displaced from this plane, as found in 1 and 2; O(1) and O(5) sit above (0.41 and 0.34 Å, respectively),³⁰ with the two symmetry equivalent O atoms correspondingly below, as also in 2. The two ethyl groups of the anion of 3b are arranged in an eclipsed fashion, this is in contrast to the staggered arrangement of these groups in the Tav analogue³¹ and both eclipsed and staggered arrangements in the V^{IV} analogue,¹⁵ although there is some disorder in the lattice water molecules.

Table 3Comparison of UV/vis absorption bands for 1, 2, 3a, 3b and $[\Delta$ -PPh4][Mo(R,R-hidpa)(R,S-hidpa)]¹⁴

Compound	Solvent	v/cm ⁻¹	ϵ/mol^{-1} dm ⁻³ cm ⁻¹
1	MeCN	18181	19
		26455	103
	CH ₂ Cl ₂	17023	47
		26774	134
2	H_2O	18181	15
		26041	61
3a	MeCN	17730	10
		26595	94
3b	H_2O	17841	13
	-	24943	61
$[PPh_4][\Delta-Mo(R,R-hidpa)-$	MeCN	18181	18
(<i>R</i> , <i>S</i> -hidpa)]		25974	89

Amavadin and its analogues crystallise with metal counter cations such as calcium and uranyl.^{5,15,32,33} The sodium cation in **3b** binds to two O(2) atoms and two O(4) atoms of the carboxylate groups from four different molybdenum-containing anions. The four oxygens are arranged around the sodium in an approximately tetrahedral manner, generating an infinite lattice; the bond lengths are 2.269(7) and 2.229(7) Å for Na–O(2) and Na–O(4), respectively, and the O–Na–O interbond angles range from 104.6(4)– $110.8(4)^\circ$.

In each case the η^2 -NO groups subtend angles at the molybdenum, see Table 2, which compare with the range 39.9–41.2° observed for related vanadium systems.^{9,11} The N–O bond lengths within these groups show a modest contraction from 1 to **3a** (Table 2), this correlates with an increase in the observed v_{N-O} stretching frequency from 1108 to 1131 cm⁻¹. For **1**, **2** and **3b** the ligating carboxylate oxygen atoms from the same ligand are mutually *trans* and occupy sites on the same side of the least-squares plane defined by the molybdenum and the four oxygen atoms; this leads to an alternating up-down pattern of these oxygen atoms with respect to the least-squares plane.

UV/Vis absorption spectra

Each compound has a brown-purple colour in solution and the electronic absorption spectra obtained for complexes 1, 2 and 3a showed a broad, low intensity, band centred at around $v = 18000 \text{ cm}^{-1}$ ($\varepsilon = 10-47 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and a more dominant feature was a medium intensity band at around v = 26000 cm^{-1} ($\varepsilon = 60-134 mol^{-1} dm^3 cm^{-1}$) (Table 3). These spectra closely resemble the UV/vis spectrum obtained for [PPh4]- $[\Delta$ -Mo(*R*,*R*-hidpa)(*R*,*S*-hidpa)].¹³ By analogy with the electronic structure proposed for Amavadin and related systems from discrete variational (DV) Xa calculations,³⁴ these transitions are assigned as $d_{x^2} \xrightarrow{} y^2 \longrightarrow d_{yz}$, d_{xz} and $d_{x^2} \xrightarrow{} y^2 \longrightarrow d_{xy}$, respectively. This interpretation suggests an "electronic equivalence" between two mutually *trans* and perpendicular η^2 -NO groups and one terminal oxo group.³⁴ The transition $d_{x^2 - y^2}$ – d_{xy} in $[M(hidca)_2]^{n-}$ (where M = V, n = 2 and M = Mo, n = 1) would be expected to be at significantly higher energy for Mo^V than V^{IV} , as shown for the comparison of d–d transitions in $[VOCl_4]^{2^-}$ and $[MoOCl_4]^{-.35}$ This transition is equivalent to 10 Dq for an octahedral complex; 10 Dq increases from 3d to 4d metals (in the same oxidation state and with the same ligands) and with increasing oxidation state. However, a similar comparison does not hold for the $d_{x^2} \xrightarrow{} v^2 \rightarrow d_{yz}$, d_{xz} transitions. Thus, the difference in energy between this band in [VOCl₄]² and in $[MoOCl_4]^{-35}$ is significantly less than the difference of ca. 6000 cm^{-1} observed between the equivalent bands of the $[V(hidca)_2]^{2-}$ and $[Mo(hidca)_2]^-$ anions, indicating that the "electronic equivalence" between M=O and $\{M = (\eta^2 - NO)_2\}$ centres is qualitative but not quantitative.³⁴ An intense charge transfer band in the region 32000-41000 cm⁻¹ was also observed in $[Mo(hidca)_2]^-$ anions. The $d_{x^2 - y^2} \rightarrow d_{z^2}$ transition is presumed to be at much higher energy than the other two d–d bands, because of ligand-field effects of molybdenum,³⁵ and hence obscured by the intense charge transfer absorptions.

EPR spectra

1, 2 and 3a all exhibit X-band EPR spectra in frozen solutions (2 in H₂O-glycerol; 1 and 3a in CH₂Cl₂-toluene) at 120 K, consistent with a Mo(v), d¹ configuration in each case with the ligand donor atoms arranged in the eight-co-ordinate geometry found in Amavadin. The spectra are either axial (2) or near axial (1, 3a) and are similar to the X-band spectrum reported for $[PPh_4][\Delta-Mo(R,R-hidpa)(R,S-hidpa)]$.¹⁴ These EPR spectra can be simulated using the spin-Hamiltonian parameters given in Table 4, and are consistent with a $d_{x^2 - y^2}$ ground state, as previously shown for the analogous V(IV) compounds.³¹ Thus, like their V(IV) counterparts, the EPR spectra of these Mo(V) complexes are indicative of the presence of a strong axial ligand field, with g_3 significantly smaller and A_3 much larger than the respective g_1, g_2, A_1 and A_2 values. The single-crystal EPR spectra of [PPh₄][Mo(hida)₂] and [Ca(H₂O)₅][V(hida)₂]·6H₂O doped in their Nb and Ti analogues, respectively, have been investigated at X-band, Q-band and 180 GHz.36 In the 180 GHz spectrum of [PPh₄][Nb{Mo}(hida)₂], all three g-features are split into two resonances, indicating the presence of two magnetically distinct species in the sample, and is assigned to the presence of two magnetically distinct, independent molecules in the asymmetric unit of [PPh4][Nb(hida)2]. These molecules have similar bond lengths and inter-bond angles. However, the dihedral angle between the two Nb- $\eta^2\text{-}NO$ groups is significantly different in the two molecules (98.3 and 95.1°). The presence of two different sets of g- and A-values is consistent with the ligand-field being dominated by the $\{M-(\eta^2-NO)_2\}$ group and hence the g- and A-values being sensitive to variations in the geometric parameters of this group.

Electrochemical studies

The redox properties of Amavadin and related systems have been explored in detail ^{7,15} and highlight the interaction between ligand and solvent in the observed $E_{1/2}$ values of the V^V/V^{IV} couple. [PPh₄][Δ -Mo(R,R-hidpa)(R,S-hidpa)]¹⁴ is capable of both a one-electron reversible oxidation and a one-electron reversible reduction in CH₂Cl₂ (Table 5). We have investigated the influence of ligand and solvent on the redox chemistry of the new eight-co-ordinate molybdenum complexes reported herein.

Fig. 4 shows the cyclic voltammograms obtained for 1 and 3a in CH₂Cl₂, where each complex exhibits a reversible Mo^{VI}/Mo^V redox couple, analogous to that of $[PPh_4][\Delta-Mo(R, R-hidpa)-$ (R,S-hidpa)].¹⁴ As with Amavadin and its relatives^{7,15} shifts of $\approx 100 \text{ mV}$ are observed in the $E_{1/2}$ value of the Mo^{VI}/Mo^V couple for the hida³⁻, hidpa³⁻ and hidba³⁻ as ligands within the same solvent system. The relative increased electron donating ability of hidba³⁻ in **3a** compared to hida³⁻ and hidpa³⁻ gives rise to the lowest $E_{1/2}$ value for the Mo^{VI}/Mo^V couple in \tilde{CH}_2Cl_2 . The trend in $E_{1/2}$ values reported for these oxidation processes is consistent with modest variations in the electron donating ability of the individual ligands and increased solubility in organic media (Table 5). The nature of the proligand also affects the Mo^V/Mo^{IV} couple of these complexes. 1 displays a quasi-reversible³⁷ Mo^V/Mo^{IV} redox couple, however, the equivalent process for 3a is irreversible (Fig. 4). The Mo^V/Mo^{IV} couple becomes less reversible on going from 1 to 2 to 3a. These electron transfer processes are considered to be metal-based as in the corresponding vanadium systems.15

A series of CPE experiments were performed for $[PPh_4]$ - $[Mo(hidpa)_2]^{14}$ in CH₂Cl₂- $[NBu^n_4][BF_4]$ (*ca.* 0.4 mol dm⁻³). The first coulometric step involved fixing the potential at +1.2 V (*vs.* SCE) and carrying out the oxidation process, thus generating Mo^{VI} by exhaustive electrolysis at 293 K. On completion the

Table 4 EPR Parameters for 1, 2, 3a and [PPh₄][Δ-Mo(R,R-hidpa)(R,S-hidpa)]

	g_3	g_1	<i>g</i> ₂	A_3/G	A_1/G	A_2/G
$[PPh_4][\Delta-Mo(R,R-hidpa)(R,S-hidpa)]^a$	1.894	1.974	1.967	86.0	29.9	35.0
1^{b}	1.893	1.976	1.969	85.0	31.0	35.0
2 ^{<i>c</i>}	1.890	1.973	1.973	86.0	34.0	34.0
$3a^b$	1.897	1.976	1.969	84.0	31.0	35.0

^{*a*} Ref. 14. ^{*b*} Dichloromethane–toluene (10 : 1) solution at 100 K. ^{*c*} Water–glycerol (10 : 1) solution at 100 K.

Table 5 $E_{1/2}$ values recorded in different solvents at a glassy carbon working electrode (*vs.* SCE) for **1**, **2**, **3a** and [PPh₄][Δ -Mo(*R*,*R*-hidpa)-(*R*,*S*-hidpa)].¹⁴ For each reversible couple the current peak intensity (i_p) obeyed a linear relationship with the square root of the scan rate (range: 20–700 mV s⁻¹)

Compound	Solvent/Electrolyte	Mo ^{VI} /Mo ^V <i>E</i> _{1/2} /V	$\Delta E/\mathrm{mV}$	i _{pa} : i _{pc}	Mo ^V /Mo ^{IV} <i>E</i> _{1/2} /V	$\Delta E/\mathrm{mV}$	i _{pa} : i _{pc}
1	CH ₂ Cl ₂ /[NBu ⁿ 4][BF4]	$+0.96^{a}$	70	0.96	-0.99°	80	1.12
2	H ₂ O/KCl	$+0.76^{b}$			_		
	Me ₂ SO/[NBu ⁿ ₄][BF ₄]	$+0.77^{a}$	70	0.94	-1.13^{b}		
3a	CH ₂ Cl ₂ /NBu ⁿ ₄ [BF ₄]	$+0.77^{a}$	70	0.95	-1.28^{b}		
$[PPh_4][\Delta-Mo(R,R-hidpa)(R,S-hidpa)]^{11}$	$CH_2Cl_2/[NBu^n_4][BF_4]$	$+0.87^{a}$	_	_	-1.12^{a}	_	_
		241.41.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4	C (1	b.	r	(O)	

^{*a*} Reversible process, the current peak intensity, i_{pa} and i_{pc} , correlated with the square root of the scan rate. ^{*b*} Irreversible process. ^{*c*} Quasi-reversible process.



Fig. 4 Cyclic voltammograms recorded at a glassy carbon electrode (*vs.* SCE) for **1** (a) and **3a** (b) (*ca.* 1 mmol dm⁻³) in CH₂Cl₂/[NBuⁿ₄][BF₄] (*ca.* 0.2 mol dm⁻³) at 293 K, scan rate = 200 mV s⁻¹.

solution became pale yellow and the cyclic voltammetric experiments were repeated using a glassy carbon working electrode. The initial oxidation-reduction profiles were observed, confirming the reversibility of the Mo^{VI}/Mo^V couple on the extended time-scale of the electrolysis experiment. A comparison of the frozen solution X-band EPR spectra before and after the electrolysis revealed a dramatic reduction in the intensity of the Mo^v resonance, consistent with the exhaustive electrolysis achieving 95% completion of oxidation to Mo^{VI}. No new signal was observed in the EPR spectra, providing clear evidence that the Mo^{VI}/Mo^V couple observed with these compounds is a metal-based one-electron transfer process. Further experiments using an OTTLE cell²² showed distinctive changes in the UV/vis absorption spectrum of [PPh4][Mo(hidpa)2] in CH₂Cl₂-[NBuⁿ₄][BF₄] (ca. 0.4 mol dm⁻³) upon gradual stepwise oxidation to +1.0 V (vs. SCE), consistent with the loss of the d-d transitions and the emergence of a charge transfer band at $v = 28000 \text{ cm}^{-1}$ ($\varepsilon = 790 \text{ mol}^{-1} \text{ dm}^{-3} \text{ cm}^{-1}$). The original spectrum containing the low intensity d-d absorption bands was observed after reduction of the solution at +0.5 V

(vs. SCE). Attempts to carry out this oxidation chemically with $[NO][BF_4]^{38}$ yielded a pale yellow product that was only sparingly soluble in CH₂Cl₂ and unstable in solvents such as MeOH and Me₂SO under anhydrous/anaerobic conditions.

A second exhaustive electrolysis experiment was carried out, by setting the potential to -1.5 V (vs. SCE), in order to produce the [Mo(hidpa)₂]²⁻ moiety. This reduction step yielded a dark red solution, however, a cyclic voltammogram of this solution revealed a loss of the original sweep profile and the only feature present was an irreversible oxidation peak at +0.56 V (vs. SCE), consistent with an electrochemical–chemical process. This illustrates that the reduced species is not stable during the coulometric experiment and undergoes chemical reaction or rearrangement, after an initial metal-based reduction process, to produce a new product that is detected by the new oxidation peak.

Comparisons of $E_{1/2}$ values recorded for Amavadin and its relatives in H₂O and Me₂SO revealed shifts of ≈500 mV for equivalent redox processes,^{6,17} highlighting the influence of hydrogen-bonding and other solvation effects in stabilising the oxidation state of these complexes. Fig. 5 shows the cyclic voltammograms obtained for 2 in H_2O and Me_2SO ; the Mo^{VI}/Mo^V redox couple is reversible in Me₂SO and irreversible in H₂O, (Table 5). This variation in the reversibility of the oxidation process, between aqueous and organic media, is in contrast to the redox chemistry of Amavadin, which displays reversible characteristics in both solvent environments,⁷ and illustrates the instability of the Mo^{VI}, d⁰, analogue in the presence of H₂O. Also in contrast to the V^{V}/V^{IV} couples with hidca³⁻ ligands, the difference in E_{pa} between H₂O and Me₂SO as solvent for **2** was only ca. 35 mV, compared to a value of ca. 500 mV for the respective V complexes. A sweep to negative potentials with 2 in H_2O revealed only a peak at -0.42 V (vs. SCE) that is due to the reduction of protons, which are present as the counter cations in 2, and this effect was also observed for Amavadin.⁷ In Me₂SO the reduction process for 2 is irreversible (Table 5), highlighting again how the solvent influences the reversibility of these redox couples.

Conclusions

The syntheses of 1, 2, 3a and 3b have further developed the chemistry of molybdenum analogues of Amavadin and X-ray crystallography has confirmed the same distinctive



Fig. 5 Cyclic voltammograms recorded at a glassy carbon electrode (vs. SCE) for 2 (a) = H_2O/KCI , (b) = $Me_2SO/[NBu^n_4][BF_4]$ (ca. 0.2 mol dm⁻³) at 293 K, scan rate = 200 mV s⁻¹.

eight-co-ordinate geometry for the molecular anions. Cyclic voltammetry has provided a wealth of information on the redox behaviour of these molybdenum complexes and further illustrated the significant role of the solvent on the electrochemical properties of members of this family of complexes. For the molybdenum complexes the Mo^V, d¹ state is significantly preferred.

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