Rhenium and molybdenum oxo-complexes containing ligands related to *N*-hydroxyiminodipropionic acid

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The reaction of *N*-hydroxy-2,2′-iminodipropionic acid with $[PPh_4][ReOBr_4]$, $[ReOCl_3(PPh_3)_2]$, $[ReOCl_2(OEt)(PPh_3)_2]$ or $[PPh_4][MoOCl_4(H_2O)]$ has produced four novel complexes: $[ReOBr_3(C_6H_8NO_5)]^-$, $[ReOBr_3(C_3H_3NO_2)]^-$, $[ReOCl_2(R,S\text{-idpa})]^-$ (H_3idpa = 2,2′-iminodipropionic acid) and $[MoO_2Cl_2(C_3H_4NO_3)]^-$. All have been successfully crystallised as their $[PPh_4]^+$ salts which have been characterised by single-crystal X-ray diffraction. The anions $[ReOBr_3(C_6H_8NO_5)]^-$ and $[ReOBr_3(C_3H_3NO_2)]^-$ involve tetragonally distorted octahedral Re^VOBr_3 (*N*,*O*) centres with the bromides *cis* to the oxo-group; $[ReOCl_2(R,S\text{-idpa})]^-$ involves a tetragonally distorted octahedral Re^VOCl_2 (*O*,*N*,*O*) centre with the 2Cl *cis* and O *trans* to the oxo-group; $[MoO_2Cl_2(C_3H_4NO_3)]^-$ involves a skew-trapezoidal $Mo^{VI}O_2Cl_2$ (*N*,*O*) centre with essentially mutual *cis* oxo-groups and *trans* chloro-groups. The dimensions of each of these co-ordination spheres are generally typical of related complexes; however, $[ReOBr_3(C_3H_3NO_2)]^-$ involves an unusually short Re–O_{oxo} bond of 1.45(4) Å. The organic moieties are considered to arise from rearrangement and/or fragmentation of *N*-hydroxy-2,2′-iminodipropionic acid, presumably under the influence of the metal centre.

Mushrooms of the genus *Amanita* accumulate vanadium to a concentration of ⩽400 mg kg^{-1} (dry weight)[1] in the form of a discrete moiety Amavadin.[2] Amavadin contains a low molecular weight 1 : 2 complex of vanadium with (*S*,*S*)-hydroxy-2,2′-iminodipropionic acid (H_3hidpa). Studies from this laboratory have established[3] that Amavadin comprises a novel eight-co-ordinate vanadium(IV) complex with two $hidpa^{3-}$ ligands, each bonded *via* an η^2-NO group and two unidentate carboxylato groups. Anderegg *et al.*[4] conducted spectrophotometric measurements on these vanadium complexes and concluded that the high stability constant ($\log_{10} \beta_2 = 23.0 \pm 1$, where $\beta_2 = [VL_2]^{2-}/[VO^{2+}][L]^2$) was due to this unusual structure and was responsible for the high selectivity of $hidpa^{3-}$ for vanadium. This high selectivity has been used as a purification step in the synthesis of $[V(hidpa)_2]^{2-}$. A crude ligand syrup of H_3hidpa (prepared from $NH_2OH{\cdot}HCl$ and 2-bromopropionic acid using a modification[5] of the procedure described by Felcman *et al.*[6]) was treated with $[VO(acac)_2]$ (acac = acetylacetonate) and which following work-up yields the desired bis(ligand) product. Further studies into the chemical nature of Amavadin have suggested that the bonding of two η^2-NO groups to the vanadium is electronically equivalent to the binding of one terminal oxo group. Thus the reactions of $[MoO_2(acac)_2]$ with the crude H_3hidpa have been investigated and the synthesis and characterisation of the molybdenum counterpart $[Mo(hidpa)_2]^-$ have been achieved.[7] The novel structure and chemical behaviour of these systems invited further development of this chemistry and following the diagonal trend of the Periodic Table we have treated H_3hidpa with oxorhenium(V) compounds to see if the chemistry and selectivity could be reproduced with this metal. Herein, we report the synthesis and structure of some new rhenium and molybdenum complexes obtained by treating H_3hidpa with oxometal complexes; these new systems involve fragments of H_3hidpa complexed to the metal centre.

Experimental

Apparatus and reagents

Solvents were used as supplied or distilled under dinitrogen using standard methods. Chemicals were obtained from either Aldrich Chemical Company Ltd. or Janssen Chimica, and used as supplied unless stated otherwise. The salt $[PPh_4][ReOBr_4]$ was prepared using the method of Cotton and Lippard[8] and $[ReOCl_3(PPh_3)]$ by the method of Chatt and Rowe.[9] The compound H_3hidpa was synthesized using a modification[5] of the procedure described by Felcman *et al.*[6] The crude H_3hidpa prepared by this route was used in the reactions with $[PPh_4]$-$[ReOBr_4]$ and $[ReOCl_3(PPh_3)_2]$. That used in the reactions with $[PPh_4][MoOCl_4(H_2O)]$ and $[ReOCl_2(OEt)(PPh_3)_2]$ was purified using the procedure of Koch *et al.*[10] The purified ligand was shown by microanalysis, ^1H and ^{13}C NMR spectroscopies to contain only H_3hidpa but as an equimolar mixture of *R*,*R* and *S*,*S* to *R*,*S* isomers. The salt $[PPh_4][MoOCl_4(H_2O)]$ was prepared by the method of Garner *et al.*[11] and $[ReOCl_2(OEt)$-$(PPh_3)_2]$ by that of Johnson *et al.*[12]

Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrometer for samples contained in a KBr matrix, far-IR spectra on a Bruker IFS66 equipped with mylar beam splitter, negative-ion FAB mass spectra using a Kratos Concept 1S spectrometer with *m*-nitrobenzyl alcohol as matrix and electronic spectra on a Shimadzu UV-260 spectrophotometer.

Syntheses

$[PPh_4][ReOBr_3(C_6H_8NO_5)]$ 1. The salt $[PPh_4][ReOBr_4]$ (0.172 g, 0.2 mmol) and crude H_3hidpa (0.075 g as a yellow syrup) were dissolved in acetone (20 cm^3) and warmed gently for 4 h, during which time the reaction mixture became dark green. The solvent was removed under reduced pressure and the residue shaken with CH_2Cl_2–water (20 cm^3 : 20 cm^3). The green organic layer was separated and then dried over anhydrous $CaCl_2$. The solid was filtered off and the solvent evaporated under reduced pressure; this produced a green residue. This residue was dissolved in the minimum volume of dry CH_2Cl_2, transferred to a flame-sealed pipette and a layer of toluene carefully introduced. After several days of standing at room temperature a small quantity of green prismatic crystals formed. The material was characterised by X-ray crystallography (see below). IR (cm^{-1}, KBr disc): 1684, 1639 (C=O), 1618 (C=N), 1386 (C–O) and 990 (Re=O). Far-IR (cm^{-1}, polythene plates): 320 (Re–O) and 227 (Re–Br). UV/VIS (CH_2Cl_2): $\tilde{\nu}/cm^{-1}$ ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 13 831 (129), 23 148 (1543), 25 316 (1558), 36 630 (7430) and 37 453 (8419).

[PPh$_4$][ReOBr$_3$(C$_3$H$_3$NO$_2$)] 2. Crude H$_3$hidpa (0.15 g as a yellow syrup) was added to a suspension of [ReOCl$_3$(PPh$_3$)$_2$] (0.333 g, 0.4 mmol) in acetone (15 cm^3) and the solution gently warmed for 4 h. A green solution and a reddish brown solid formed. The precipitate was filtered off, washed with Et$_2$O (3 × 15 cm^3), dried under vacuum and dissolved in CH$_2$Cl$_2$ (10 cm^3). Toluene (40 cm^3) was carefully layered onto the CH$_2$Cl$_2$ solution and, after several days of standing at room temperature, red tabular crystals formed which were identified by microanalysis, single-crystal X-ray diffraction and IR spectroscopy as the mixed halogeno complex [ReBr$_{2.5}$Cl$_{1.5}$(OPPh$_3$)].[13]

The solvent was evaporated under reduced pressure from the green filtrate and the residue shaken with CH$_2$Cl$_2$–water (25 cm^3 : 25 cm^3). The green aqueous layer was separated and then placed over a solution of [PPh$_4$]Br (0.167 g, 0.4 mmol) in CH$_2$Cl$_2$ (15 cm^3) and left overnight whereupon the colour had transferred from the aqueous layer to the organic layer. The organic layer was separated, dried over anhydrous CaCl$_2$ and the solvent removed under reduced pressure. The green residue was dissolved in the minimum volume of dry CH$_2$Cl$_2$ and toluene was carefully layered onto the solution. After several days of standing at room temperature a few bright green needles formed. The compound was characterised by X-ray crystallography (see below). IR (cm^{-1}, KBr disc): 1668 (C=O), 1622 (C=N), 1385 (C–O) and 987 (Re=O). Far-IR (cm^{-1}, polythene plates): 312 (Re–O) and 215 (Re–Br). Negative-ion FAB mass spectrum: *m/z* 528 {528 for [ReOBr$_3$(C$_3$H$_3$NO$_2$)]$^-$}. UV/VIS (CH$_2$Cl$_2$): $\tilde{\nu}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) 13 966 (119), 22 936 (1342), 25 189 (1492), 36 364 (6173) and 37 453 (7459).

[PPh$_4$][MoO$_2$Cl$_2$(C$_3$H$_4$NO$_3$)] 3. The salt [PPh$_4$][MoOCl$_4$(H$_2$O)] (0.306 g, 0.5 mmol) was added to a suspension of purified H$_3$hidpa (0.368 g, 1.05 mmol) in tetrahydrofuran (thf) (20 cm^3) and stirred under a dinitrogen atmosphere for 24 h. A bright yellow solution was produced which was filtered and evaporated to dryness. The resultant residue was extracted into CH$_2$Cl$_2$ (10 cm^3) and the product precipitated by adding Et$_2$O (20 cm^3). The yellow precipitate was collected and dried under vacuum. Yellow prismatic crystals were produced by layering the minimum volume CH$_2$Cl$_2$ solution of the product with toluene. Yield 0.250 g, 39% (Found: C, 50.7; H, 3.8; Cl, 11.2; Mo, 14.7; N, 2.0; P, 4.4. Calc. for C$_{27}$H$_{24}$Cl$_2$MoNO$_5$P: C, 50.6; H, 3.8; Cl, 11.1; Mo, 14.9; N, 2.2; P, 4.8%). IR (cm^{-1}, evaporated film): 1643 (C=O), 947 (Mo=O$_{\mathrm{sym}}$) and 908 (Mo=O$_{\mathrm{asym}}$).

[PPh$_4$][ReOCl$_2$(*R*,*S*-idpa)] 4. Purified H$_3$hidpa (0.354 g, 2 mmol) and [PPh$_4$]Cl (0.384 g, 1 mmol) were added to a suspension of [ReOCl$_2$(OEt)(PPh$_3$)$_2$] (0.842 g, 1 mmol) in acetone (20 cm^3), and the mixture stirred for 2 h, which produced a green solution. This solution was filtered and evaporated to dryness under reduced pressure. The residue was extracted with CH$_2$Cl$_2$–water (25 cm^3 : 25 cm^3), the organic layer was separated and dried over anhydrous CaCl$_2$, filtered and the solvent removed under reduced pressure. Pale green crystals were produced by introducing a layer of Et$_2$O onto the minimum volume CH$_2$Cl$_2$ solution of the solid. Yield 0.485 g, 63% (Found: C, 46.2; H, 3.6; N, 1.7. Calc. for C$_{30}$H$_{28}$Cl$_2$NO$_5$PRe: C, 46.5; H, 3.7; N, 1.8%). Negative-ion FAB mass spectrum: *m/z* 432 {432 for [ReOCl$_2$(idpa)]$^-$}. IR (cm^{-1}, KBr disc): 1701, 1649 (C=O), 1385 (C–O), 980 (Re=O) and 316 (Re–O). UV/VIS (CH$_2$Cl$_2$): $\tilde{\nu}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) 13 889 (36.3), 23 981 (sh, 12.4), 28 249 (32.2), 36 364 (3483) and 37 453 (4362).

Crystallography

A summary of the crystallographic data is provided in Table 1. All data collected were corrected for Lorentz-polarisation effects and empirical absorption corrections were applied using the program DIFABS[14] (compound **1**) or based on azimuthal scans of several reflections (compounds **2**, **3** and **4**). All of the structures were solved by direct methods.[15] Hydrogen atoms were included in the structure-factor calculations in idealised positions (C–H 0.95 Å) and were assigned isotropic thermal parameters which were 20% greater than the equivalent *B* value of the atom to which they were bonded. The final cycle of full-matrix least squares, $\Sigma w(|F_o| - |F_c|)^2$, was based on the observed reflections [$I > 3.00\sigma(I)$] and the number of variable parameters, using neutral atom scattering factors and anomalous dispersion corrections.[16] All calculations were performed using the TEXSAN[17] crystallographic software package. Crystals of compounds **1** and **3** were mounted on a glass fibre and all non-hydrogen atoms were refined anisotropically. Crystallisation of compound **2** gave a few, very thin needle crystals, which were weakly diffracting. Of these several were mounted and tested for possible data collection. The best crystal was then selected for full crystal-structure analysis. Owing to the low proportion of observed data, only the rhenium, bromine and phosphorus atoms were refined anisotropically, all other non-hydrogen atoms being refined isotropically. Crystals of compound **4** were thin needles sensitive to solvent loss. Several were selected, mounted in sealed glass capillaries and tested for possible data collection. The best crystal was identified for full crystal-structure analysis. Two water molecules which showed high thermal motion were observed in the asymmetric unit and these were refined isotropically. All other non-hydrogen atoms were refined anisotropically.

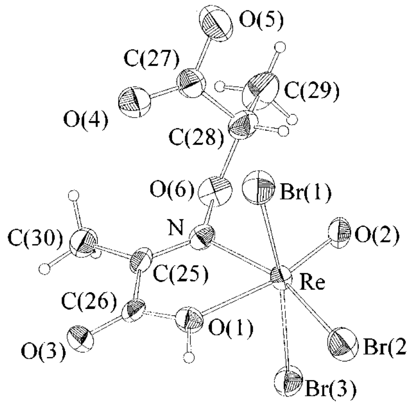

Fig. 1 An ORTEP[18] view showing the anion of [PPh$_4$][ReOBr$_3$(C$_6$H$_8$NO$_5$)] **1**

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/550.

Discussion

Structure of [PPh$_4$][ReOBr$_3$(C$_6$H$_8$NO$_5$)] 1

This compound contains discrete [PPh$_4$]$^+$ cations and [ReOBr$_3$(C$_6$H$_8$NO$_5$)]$^-$ anions. The structure of the anion is shown in Fig. 1 and the metal–ligand and some intraligand bond lengths and angles are given in Table 2. Rhenium is bound to a terminal oxygen [O(2)], three *cis*-bromine atoms, and the ligand (C$_6$H$_8$NO$_5$)$^-$, 2-[(1-carboxyethoxy)imino]propionic acid. Fig. 2 shows a schematic representation of the ligand, which binds through the nitrogen *cis* to the Re–O$_{\mathrm{oxo}}$ group and one unidentate carboxylic acid oxygen [O(1)] *trans* to O(2). The diffraction data showed the bound carboxylate oxygen O(1) to be protonated in the solid state [O(1)–H(1) 1.034 Å] and that N is double bonded to C(25) [N–C(25) 1.28(1) Å, Re–N–O(6) 122.8(6), Re–N–C(25) 121.3(7), O(6)–N–C(25) 115.1(8)°]. The O(4)–C(27) bond length of 1.20(1) Å is indicative of a double

Table 1 Crystallographic data for $[PPh_4][ReOBr_3(C_6H_8NO_5)]$ **1**, $[PPh_4][ReOBr_3(C_3H_3NO_2)]$ **2**, $[PPh_4][MoO_2Cl_2(C_3H_4NO_3)]$ **3** and $[PPh_4][ReOCl_2(R,S\text{-idpa})]$ **4**

	1	**2**	**3**	**4**
Empirical formula	$C_{30}H_{28}Br_3NO_6PRe$	$C_{27}H_{24}Br_3NO_3PRe$	$C_{27}H_{24}Cl_2MoNO_5P$	$C_{30}H_{28}Cl_2NO_5PRe$
M	955.45	867.38	715.83	770.64
Crystal colour, habit	Green, prismatic	Green, acicular	Pale yellow, prismatic	Green, prismatic
Crystal dimensions/mm	0.15 × 0.15 × 0.45	0.05 × 0.10 × 0.35	0.25 × 0.30 × 0.55	0.02 × 0.10 × 0.35
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
a/Å	9.324(2)	9.399(3)	27.385(4)	26.422(2)
b/Å	11.588(2)	10.65(2)	28.395(4)	26.348(4)
c/Å	30.478(5)	14.640(4)	7.070(4)	9.869(2)
β/°	94.10	97.16(3)		
U/Å^3	3285(1)	1454(2)	5497(2)	6871(3)
Space group	$P2_1/c$ (no. 14)	$P2_1$ (no. 14)	$P2_12_12$ (no. 18)	*Pbca* (no. 61)
Z	4	2	8	8
D_c/g cm^{-3}	1.932	1.982	1.730	1.490
μ/cm^{-1}	Cu-Kα, 121.17	Mo-Kα, 84.02	Cu-Kα, 76.62	Cu-Kα, 88.64
Diffractometer	Rigaku AFC 5R	Rigaku AFC 6S	Rigaku AFC 5R	Rigaku AFC 5R
Radiation (λ/Å)	Cu-Kα (1.541 78)	Mo-Kα (0.710 69)	Cu-Kα (1.541 78)	Cu-Kα (1.541 78)
T/°C	22	21	21	20
Scan type	ω	ω–2θ	ω–2θ	ω–2θ
Scan rate/° min^{-1} in ω	32.0 (2 rescans)	2.0 (3 rescans)	16.0	8.0 (2 rescans)
Scan width	1.34 + 0.30 tan θ	1.31 + 0.30 tan θ	1.31 + 0.30 tan θ	1.26 + 0.30 tan θ
$2\theta_{max}$/°	120.1	50.0	120.0	120.2
Decay (% decline)	−0.20	−0.80	−3.10	−3.17
No. reflections measured	Total 5528 Unique 5170 (R_{int} = 0.058)	Total 3171 Unique 2718 (R_{int} = 0.426)	Total 4649	Total 5721
No. observations [$I > 3.00\sigma(I)$]	3878	1484	4010	3337
No. variables	379	169	666	369
Residuals: *R*, *R′*	0.045, 0.062	0.091, 0.111	0.052, 0.064	0.080, 0.101
Goodness of fit	1.96	3.44	2.26	2.97

Table 2 Selected bond distances (Å) and angles (°) for $[PPh_4][ReOBr_3(C_6H_8NO_5)]$ **1** and $[PPh_4][ReOBr_3(C_3H_3NO_2)]$ **2**

$[PPh_4][ReOBr_3(C_6H_8NO_5)]$ **1**		$[PPh_4][ReOBr_3(C_3H_3NO_2)]$ **2**	
Re–Br(1)	2.507(1)	Re–Br(1)	2.501(9)
Re–Br(2)	2.436(1)	Re–Br(2)	2.488(9)
Re–Br(3)	2.519(1)	Re–Br(3)	2.422(9)
Re–O(1)	2.058(7)	Re–O(1)	1.93(5)
Re–O(2)	1.666(7)	Re–O(3)	1.45(4)
Re–N	2.146(8)	Re–N	2.14(3)
O(6)–N	1.42(1)	N–C(26)	1.12(6)
O(6)–C(28)	1.28(1)	O(1)–C(25)	1.32(6)
N–C(25)	1.28(1)	O(2)–C(25)	1.22(6)
O(4)–C(27)	1.20(1)	C(25)–C(26)	1.52(8)
O(5)–C(27)	1.31(1)		
Br(1)–Re–Br(2)	89.07(5)	Br(1)–Re–Br(2)	166.8(3)
Br(1)–Re–Br(3)	170.12(5)	Br(1)–Re–Br(3)	88.5(4)
Br(1)–Re–O(1)	86.0(2)	Br(1)–Re–O(1)	75.0(1)
Br(1)–Re–O(2)	95.8(2)	Br(1)–Re–O(3)	111.0(2)
Br(1)–Re–N	90.9(2)	Br(1)–Re–N	89.2(9)
Br(2)–Re–Br(3)	88.24(5)	Br(2)–Re–Br(3)	86.2(9)
Br(2)–Re–O(1)	91.9(2)	Br(2)–Re–O(1)	93.0(1)
Br(2)–Re–O(2)	106.6(2)	Br(2)–Re–O(3)	82.0(2)
Br(2)–Re–N	162.9(2)	Br(2)–Re–N	91.9(9)
Br(3)–Re–O(1)	84.6(2)	Br(3)–Re–O(1)	95.0(1)
Br(3)–Re–O(2)	94.1(2)	Br(3)–Re–O(3)	102.0(2)
Br(3)–Re–N	88.8(2)	Br(3)–Re–N	164.6(9)
O(1)–Re–O(2)	161.4(3)	O(1)–Re–O(3)	162.0(2)
O(1)–Re–N	71.0(3)	O(1)–Re–N	70.0(1)
O(2)–Re–N	90.3(3)	O(3)–Re–N	93.0(2)
Re–N–O(6)	122.8(6)	Re–N–C(26)	125.0(4)
Re–N–C(25)	121.3(7)		
O(6)–N–C(25)	115.1(8)		

bond, whilst the O(5)–C(27) bond length of 1.31(1) Å implies single-bond character. No hydrogen atom was found, from the diffraction data, to be bonded to either of the non-bonded carboxylate oxygen atoms O(4) or O(5). The overall charge on the $C_6H_8NO_5$ group is considered to be 1− and thus $[ReOBr_3(C_6H_8NO_5)]^-$ is regarded as involving Re^V. This assignment of oxidation state is further supported by the lack of an EPR signal, which is consistent with d^2 in an axial field for Re^V.[19]

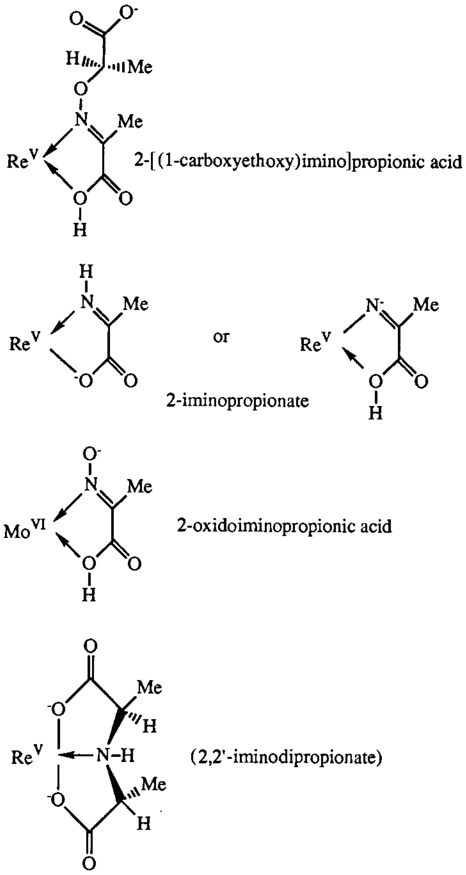

Fig. 2 Schematic representations of the ligands of the four compounds $[PPh_4][ReOBr_3(C_6H_8NO_5)]$ **1**, $[PPh_4][ReOBr_3(C_3H_3NO_2)]$ **2**, $[PPh_4][MoO_2Cl_2(C_3H_4NO_3)]$ **3** and $[PPh_4][ReOCl_2(R,S\text{-idpa})]$ **4**

The asymmetric carbon C(28) is shown in the *S* configuration. However, the crystals are refined in the achiral space group, $P2_1/c$, showing that both *S* and *R* chiralities are present in the unit cell. A least-squares best plane of the chelating ring

ReO(1)C(26)C(25)N shows that it is approximately planar, with maximum deviations of 0.066 Å below the plane [*i.e.* towards Br(1)] for N and 0.062 Å above the plane for C(26). The oxygen atom [O(1)] of the chelate binds *trans* to the O_{oxo} group, O(1)–Re–O(2) 161.4(3)°. The occurrence of the *trans* RO–Re–O_{oxo} arrangement in six-co-ordinate rhenium(V) compounds is well documented.[20–22] The Re^{V}–N bond distance [2.146(8) Å] is significantly longer than the Re^{V}–O(1) bond distance [2.058(7) Å], consistent with the observations of Mazzi and co-workers.[20,21] These authors[21] report that for quasi-octahedral $Re^{V}O$ complexes with oxygen-containing bidentate ligands there is a clear preference for the *trans* O=Re–OR configuration. They suggest that this configuration corresponds to a minimum of *trans* weakening caused by the Re=O multiple bond. Secondly they stated that the repulsion exerted by the O_{oxo} atom causes a compression field which tends to increase the mean O_{oxo}=Re–L_{cis} angle beyond 90°. A least-squares plane defined by the atoms NBr(1)Br(2)Br(3) shows that the three bromine atoms sit approximately in the plane, the nitrogen atom sits 0.217 Å below the plane [*i.e.* away from the oxygen O(2)] and the rhenium atom is 0.212 Å above the plane. The dihedral angle between this plane and that defined by the chelate ring ReO(1)C(26)C(25)N is 91.69°.

The co-ordination geometry around the rhenium is tetragonally distorted octahedral. The metal–ligand bond distances (Table 2) agree well with those observed in other rhenium(V) quasi-octahedral oxo-complexes.[20–24] The Re–O(2)$_{oxo}$ distance of 1.666(7) Å is comparable with those for other Re–O_{oxo} bonds, *e.g.* 1.652(8) Å, 1.680(7) Å and 1.685(8) Å in [ReOCl(PMe$_2$Ph)L^1],[20] [HL^1 = *N*-(2-hydroxyphenyl)salicylideneamine], [ReOCl$_2${OC$_6$H$_4$[CH$_2$NH(CH$_2$)$_3$PPh$_2$]-2}][24] and [ReOCl$_2$(PPh$_3$){Ph(O)CNNCMe$_3$}],[23] respectively. The high π-electron density due to the short Re–O_{oxo} bond causes an increase in the O_{oxo}–Re–L_{cis} angle beyond 90°. This is particularly noticeable for the O_{oxo}–Re–Br bond angles [Br(1)–Re–O(2) 95.8(2), Br(2)–Re–O(2) 106.6(2) and Br(3)–Re–O(2) 94.1(2)°] consistent with the observations of Mazzi and co-workers.[21] The distortion of the Re–Br bonds away from the Re–O_{oxo} bond is probably facilitated by the displacement of O(1) due to the restricted bite of the chelate [N–Re–O(1) 71.0(3) and O(1)–Re–O(2) 161.4(3)°]. Similar deviations from regular octahedral geometry have been observed in other oxohalogeno rhenium(V) complexes; for example, O_{oxo}–Re–Cl_{cis} 102.6° in [ReO(Cl)L$^2_2$][25] (HL^2 = *N*-methylsalicylideneamine) and O_{oxo}–Re–Cl_{cis} 101.9(3) and 97.5(3)° in [ReOCl$_2${OC$_6$H$_4$-[CH$_2$NH(CH$_2$)$_3$PPh$_2$]-2}].[24]

Compound **1** prepared from [PPh$_4$][ReOBr$_4$], as characterised by X-ray crystallography, has retained three bromine atoms and an oxo group at the metal centre. The novel ligand moiety 2-[(1-carboxyethoxy)imino]propionic acid is bound through the nitrogen and one unidentate carboxylate group. The second carboxylate group has remained unbound. The infrared spectrum shows $\nu_{C=O}$ at 1684 and 1639 cm^{-1}. A comparison with bis(glycinato) complexes[26] suggested that the band at 1684 cm^{-1} was due to the asymmetric $\nu_{C=O}$ from the unidentate co-ordinated CO$_2$(Re) group and that the band at 1639 cm^{-1} was from the asymmetric $\nu_{C=O}$ of the unbound deprotonated carboxylate group. A weak band at 1618 cm^{-1} was assigned to $\nu_{C=N}$ from a comparison with the complexes *trans*-[ReOBr$_2$(L^2)(PPh$_3$)] and *trans*-[ReOBr$_2$(L^3)(PPh$_3$)][27] (HL^3 = *N*-phenylsalicylideneamine), where $\nu_{C=N}$ was at 1612 and 1605 cm^{-1}, respectively. The ν_{C-O} is assigned at 1386 cm^{-1} following Nakamoto,[26] although it is worth noting that Roncari *et al.*[27] reported this stretch to be at 1284 cm^{-1} for the complex *trans*-[ReOBr$_2$(L^2)(PPh$_3$)] and a second band in this region was observed at 1258 cm^{-1} for **1**. The $\nu_{Re=O}$ is assigned at 990 cm^{-1}. The far-infrared spectrum shows a broad band at 227 cm^{-1}, assigned to ν_{Re-Br} {210, 216 and 202 cm^{-1} for *trans*-[ReOBr$_2$(L^2)(PPh$_3$)], *trans*-[ReOBr$_2$(L^3)(PPh$_3$)] and *trans*-[ReOBr$_2$(quin)(PPh$_3$)],[27] (Hquin = quinolin-8-ol) respectively} and a sharper band at 320 cm^{-1}, ascribed to ν_{Re-O} vibration.[26]

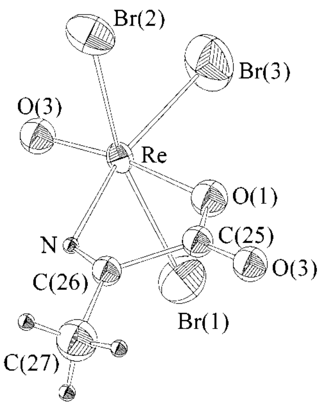

Fig. 3 An ORTEP view showing the anion of [PPh$_4$][ReOBr$_3$-(C$_3$H$_3$NO$_2$)] **2**

Structure of [PPh$_4$][ReOBr$_3$(C$_3$H$_3$NO$_2$)] 2

This compound consists of discrete [PPh$_4$]$^+$ cations and [ReOBr$_3$(C$_3$H$_3$NO$_2$)]$^-$ anions. The crystal structure shows that halide exchange has taken place, with the chlorides in the original [ReOCl$_3$(PPh$_3$)$_2$] being displaced by residual bromide in the crude ligand mixture or from [PPh$_4$]Br. The structure of the anion is shown in Fig. 3 and the metal–ligand bond distances and selected ligand bond lengths and angles are given in Table 2. The crystal structure determination serves to characterise the chemical nature of the anion. However, due to the high *R* factors ($R = 0.091$ and $R' = 0.111$) and large estimated standard deviations for the dimensions of this molecule, it should be considered in a qualitative rather than a quantitative manner. The geometry at the metal is irregular octahedral, but there is an uncertainty in the charge associated with the organic ligand and hence the oxidation state of the metal. From the short N–C(26) distance, 1.12(6) Å, the Re–N–C(26) bond angle, 125.0(4)°, and angles around the C(26) carbon, N–C(26) is considered to be a double bond. Therefore, the 2-iminopropionate ligand appears to be dinegative, which would indicate a rhenium(VI) species. However, the electronic absorption spectrum and lack of an EPR signal are more consistent with Re^{V}. Comparison with **1** suggests that the chelate oxygen, O(1), could be protonated, alternatively N could be protonated. The lack of evidence for the proton on either O(1) or N is not unexpected, given the high *R* factors for this structure determination and the ‘electron rippling’ effect close to the rhenium atom, which would mask any hydrogen atoms near to the metal. It is worth noting that the complex [Co(NH$_3$)$_4${N(H)=C-(CH$_3$)C(O)O}]$^{2+}$ has been synthesized and that the authors[28] reported that the metal imine group is highly acidic and the proton very labile.

The co-ordination around the rhenium atom in compound **2** (Fig. 3) is similar to that of other related rhenium(V) complexes, including **1** (Fig. 1). The rhenium is bound to a terminal oxygen [O(3)], three *cis*-bromine atoms, and the *N*,*O* chelate (C$_3$H$_3$NO$_2$)$^-$, 2-iminopropionate (Fig. 2), with O(1) *trans* to the oxo-group [O(3)]. As in [ReOBr$_3$(C$_6$H$_8$NO$_5$)]$^-$, the Re–N bond distance of [ReOBr$_3$(C$_3$H$_3$NO$_2$)]$^-$ is expected to be longer [Re–N 2.14(3), *cf.* 2.146(8) Å] than the Re–O(1) bond distance [1.93(5) Å, *cf.* 2.058(7) Å] consistent with the observations of Mazzi and co-workers.[20,21] This Re–O(1) bond distance is relatively short, demonstrating an absence of significant *trans* lengthening. However, this lack of any obvious *trans* lengthening is not unknown[21] and is observed for the complex *trans*-[ReOBr$_2$(PPh$_3$)L^4][20] (HL^4 = salicylideneamine) where Re–O_{trans} [1.937(5) Å] is shorter than the Re–O_{cis} distances found in

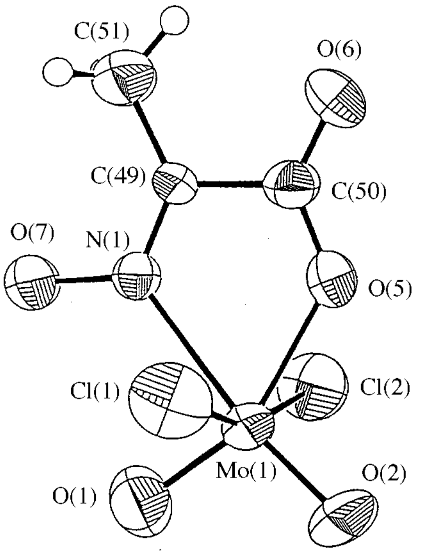

Fig. 4 An ORTEP view showing the anion of [PPh$_4$][MoO$_2$Cl$_2$(C$_3$H$_4$NO$_3$)] **3**

[ReO(Cl)L$^2{}_2$][21] and [ReOCl$_2$(PPh$_3$)(acac)$_2$][21] [1.995(4) and 1.99(1) Å, respectively]. The lack of *trans* lengthening is also consistent with Re^V, whereby in the bonding of *trans* d^2 MO$_2$ systems both d electrons will occupy the formally non-bonding 'in plane' d$_{xy}$ orbital, giving less repulsion in the axial direction and optimising the O p$_\pi$–M d$_\pi$ interaction. The least-squares plane for $\overline{\mathrm{ReO(1)C(25)C(26)N}}$ in **2** shows some distortion, the oxygen O(1) being 0.089 Å above the plane [towards Br(2)] and the carbon C(25) 0.101 Å below the plane; this is in contrast to **1** where the chelating ring is essentially planar. The terminal oxygen–rhenium bond distance [Re=O(3) 1.45(4) Å] is exceptionally short. A search of the Cambridge Crystallographic Database using Quest,[29] revealed only three Re–O$_{oxo}$ bonds shorter than 1.5 Å and all of these are in rhenate anions: bis[1,2-bis(diphenylphosphino)ethane]dioxorhenium perrhenate (Re=O 1.455 Å),[30] pentakis(dimethyl sulfoxide)oxovanadium rhenate (Re=O 1.434 Å and 1.478 Å).[31] Two of the O$_{oxo}$–Re–Br angles are greater than 90° [Br(1)–Re–O(3) 111.0(2), Br(3)–Re–O(3) 102(2)°] while the Br(2)–Re–O(3) angle is 82.0(2)°, in contrast to **1** where all three Br–Re–O$_{oxo}$ angles are greater than 90°. The chelate has a restricted bite as also seen for **1**, N–Re–O(1) 70(1)°, and this seems to have the major effect on the position of O(1), O(1)–Re–O(3): 162.0(2)° [*cf.* N(1)–Re–O(1) 71.0(3) and O(1)–Re–O(2) 161.4(3)° in **1**]. The atoms NBr(1)Br(2)Br(3) are essentially planar and the rhenium atom is 0.282 Å above this plane [towards O(3)], which is inclined at 83.8° to the least-squares plane of $\overline{\mathrm{ReO(1)C(25)C(26)N}}$.

The compound **2**, as characterised by single-crystal X-ray analysis, showed that halide exchange occurred on the 'ReOCl$_3$' moieties, with the three chlorine atoms being replaced by three bromine atoms. The two PPh$_3$ groups in the starting material have been formally replaced by the new ligand fragment 2-iminopropionate. The IR spectrum showed $\nu_{C=O}$ at 1668 cm^{-1}, only a single band being observed, reflecting the presence of a single type of carboxylate group. The frequency of this band compares with that observed for $\nu_{C=O}$ of **1** (1684 cm^{-1}), assigned to the bound CO$_2$(Re) group. A weak band at 1622 cm^{-1} is assigned to $\nu_{C=N}$,[27] ν_{C-O} is observed at 1385 cm^{-1} and $\nu_{Re=O}$ at 987 cm^{-1} (*cf.* 1618, 1386 and 990 cm^{-1} for **1**). The far-IR spectrum showed the presence of two bands as was observed for **1**, a broad band at 215 cm^{-1} assigned to ν_{Re-Br}[27] and a sharp band at 312 cm^{-1} assigned to ν_{Re-O}.[26] The negative-ion FAB mass spectrum showed the parent ion at *m/z* 528 with the appropriate isotopic splitting pattern.

Table 3 Selected bond lengths (Å) and interbond angles (°) in the anion of [PPh$_4$][MoO$_2$Cl$_2$(C$_3$H$_4$NO$_3$)] **3**

Mo(1)–Cl(1)	2.386(3)	Mo(2)–Cl(3)	2.375(3)
Mo(1)–Cl(2)	2.377(3)	Mo(2)–Cl(4)	2.380(3)
Mo(1)–O(1)	1.668(9)	Mo(2)–O(3)	1.699(9)
Mo(1)–O(2)	1.675(7)	Mo(2)–O(4)	1.687(8)
Mo(1)–O(5)	2.121(8)	Mo(2)–O(8)	2.124(8)
Mo(1)–N(1)	2.342(8)	Mo(2)–N(2)	2.350(8)
O(5)–C(50)	1.28(1)	O(8)–C(53)	1.27(1)
O(6)–C(50)	1.20(1)	O(9)–C(53)	1.23(1)
O(7)–N(1)	1.35(1)	O(10)–N(2)	1.35(1)
N(1)–C(49)	1.24(1)	N(2)–C(52)	1.27(1)
Cl(1)–Mo(1)–Cl(2)	160.1(1)	Cl(3)–Mo(2)–Cl(4)	160.6(1)
Cl(1)–Mo(1)–O(1)	94.0(3)	Cl(3)–Mo(2)–O(3)	93.9(3)
Cl(1)–Mo(1)–O(2)	99.2(3)	Cl(3)–Mo(2)–O(4)	98.6(4)
Cl(1)–Mo(1)–O(5)	82.5(2)	Cl(3)–Mo(2)–O(8)	83.1(2)
Cl(1)–Mo(1)–N(1)	81.5(2)	Cl(3)–Mo(2)–N(2)	81.5(2)
Cl(2)–Mo(1)–O(1)	93.6(3)	Cl(4)–Mo(2)–O(3)	93.8(3)
Cl(2)–Mo(1)–O(2)	96.5(3)	Cl(4)–Mo(2)–O(4)	96.4(4)
Cl(2)–Mo(1)–O(5)	82.9(2)	Cl(4)–Mo(2)–O(8)	82.4(2)
Cl(2)–Mo(1)–N(1)	80.9(2)	Cl(4)–Mo(2)–N(2)	81.4(2)
O(1)–Mo(1)–O(2)	104.7(5)	O(3)–Mo(2)–O(4)	105.6(5)
O(1)–Mo(1)–O(5)	155.0(4)	O(3)–Mo(2)–O(8)	155.0(3)
O(1)–Mo(1)–N(1)	85.0(4)	O(3)–Mo(2)–N(2)	85.3(4)
O(2)–Mo(1)–O(5)	100.3(4)	O(4)–Mo(2)–O(8)	99.4(4)
O(2)–Mo(1)–N(1)	170.2(5)	O(4)–Mo(2)–N(2)	169.1(4)
O(5)–Mo(1)–N(1)	70.0(3)	O(8)–Mo(2)–N(2)	69.7(3)
Mo(1)–N(1)–O(7)	125.0(6)	Mo(2)–N(2)–O(10)	124.9(6)
Mo(1)–N(1)–C(49)	118.6(7)	Mo(2)–N(2)–C(52)	117.9(8)
O(7)–N(1)–C(49)	116.3(8)	O(10)–N(2)–C(52)	117.0(8)

Structure of [PPh$_4$][MoO$_2$Cl$_2$(C$_3$H$_4$NO$_3$)] 3

The molecular structure of the anion [MoO$_2$Cl$_2$(C$_3$H$_4$NO$_3$)]$^-$ is shown in Fig. 4 and selected bond lengths and angles are listed in Table 3. There are two independent [MoO$_2$Cl$_2$(C$_3$H$_4$NO$_3$)]$^-$ anions in the asymmetric unit which are essentially identical. One [PPh$_4$]$^+$ counter ion is in a general position, the other is shared by two (two-fold) sites. The molybdenum atom is bonded to two terminal oxygen atoms, two terminal chlorine atoms and to the fragment (O)N=C(Me)CO$_2$H, 2-oxidoiminopropionic acid (see Fig. 2) through the nitrogen and a unidentate carboxylate oxygen atom. The two terminal oxygen atoms are *cis* to each other while the chlorine atoms are *trans* to each other. The nitrogen (N) is bound *trans* to the O(2) oxygen and the carboxylate oxygen atom [O(5)] *trans* to the O(1) oxo group.

The ligand C$_3$H$_4$NO$_3$ fragment forms a $\overline{\mathrm{Mo(1)O(5)C(50)C(49)N(1)}}$ chelate ring with a restricted bite angle, O(5)–Mo(1)–N(1) 70(3)°, and the chelating ring is essentially planar as shown by least-squares analysis, with maximum deviations above the plane [*i.e.* towards Cl(1)] of 0.0113 Å for N(1) and 0.0233 Å below the plane for C(49). The composition of the ligand fragment, 2-oxidoiminopropionic acid, is shown in Fig. 2. A proton was located by the crystallographic analysis on the bound carboxylate oxygen [O(5)], N(1) is doubly bonded to C(49) [N(1)–C(49) 1.24(1) Å], the O(6)–C(50) bond length of 1.20(1) Å is indicative of a double bond, the N(1)–O(7) distance of 1.35(1) Å suggests a single bond and because there is no proton evident from the X-ray diffraction data a negative charge is assigned to the O(7) oxygen. Therefore, an overall charge of 1− on the ligand is suggested. This 1− charge, the formula of the anion, and the presence of one [PPh$_4$]$^+$ per anion leads to the complex being regarded as involving Mo^{VI}. The IR spectrum gives further credence to this view and the lack of an EPR signal confirms the assignment.

The skew trapezoidal arrangement with the terminal oxygen atoms *cis* to each other and the chlorine atoms mutually *trans* to each other has been observed for several other systems.[32,33] The Mo(1)–O(5) bond length [2.121(8) Å] is comparable to those of other molybdenum(VI) complexes.[34–36] The

Table 4 Rhenium–ligand bond distances (Å) and interbond angles (°) in $[PPh_4][ReOCl_2(R,S\text{-idpa})]$ **4**

Re–Cl(1)	2.334(5)	Re–O(2)	2.05(1)
Re–Cl(2)	2.401(5)	Re–O(3)	2.02(1)
Re–O(1)	1.66(1)	Re–N	2.17(1)
Cl(1)–Re–N	162.1(4)	Cl(2)–Re–O(1)	95.6(5)
Cl(2)–Re–O(2)	83.7(4)	Cl(2)–Re–O(3)	166.7(4)
Cl(2)–Re–N	98.3(3)	O(1)–Re–O(2)	165.0(5)
O(1)–Re–O(3)	97.7(6)	O(1)–Re–N	90.4(5)
O(2)–Re–O(3)	83.4(5)	O(2)–Re–N	75.0(5)
O(3)–Re–N	81.1(5)		

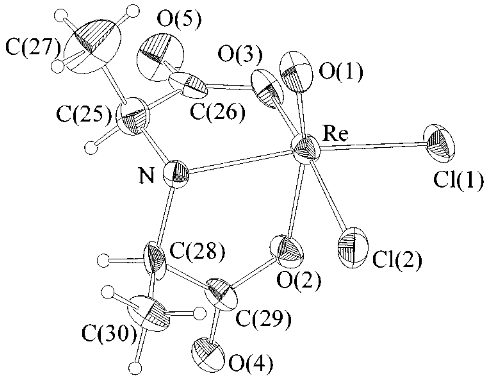

Fig. 5 An ORTEP view showing the anion of $[PPh_4][ReOCl_2(R,S\text{-idpa})]$ **4**

Mo(1)–N(1) bond length, 2.342(8) Å, is long though not uncommon for nitrogen atoms bound *trans* to a terminal oxygen, *cf*. Mo–N 2.342(3) Å in $[MoO_2\{HOC_2H_4N(C_2H_4O)_2\}]$,[34] 2.299(3) Å in $[NMe_4][MoO_2(L^5)]$ [L^5 = 2-(salicylideneamino)-benzenethiolate][35] and 2.308(3) Å in $[MoO_2Cl_2(C_{12}H_8N_2)]$.[32]

Therefore, the reaction of $[PPh_4][MoOCl_4(H_2O)]$ with purified H_3hidpa results in the complex anion **3** in distorted octahedral conformation. The molybdenum atom is bound to two terminal oxygen atoms, two chlorine atoms and the ligand fragment $(O)N{=}C(Me)CO_2H^-$ through the nitrogen and one unidentate carboxylate oxygen. The IR spectrum shows $\nu_{C=O}$ at 1643 cm^{-1}, $\nu(Mo{=}O_{sym})$ at 947 cm^{-1} and $\nu(Mo{=}O_{asym})$ at 908 cm^{-1}. The Mo=O symmetric and asymmetric stretching values are typical for dioxodihalogenomolybdenum(VI) complexes.[37]

Structure of $[PPh_4][ReOCl_2(R,S\text{-idpa})]$ 4

The molecular structure of the anion of complex **4** is shown in Fig. 5 and the metal–ligand bond lengths and selected bond angles within the anion are shown in Table 4. The rhenium is bound to a terminal oxygen atom O(1), to two chlorine atoms *cis* to O(1) and to each other and to a 2,2′-iminodipropionate(2−) ($idpa^{2-}$) ligand through two unidentate carboxylate oxygen atoms [O(2) and O(3)] and the nitrogen N. The carboxylate oxygen atom O(2) is bound *trans* to O(1). The compound *R*,*S*-H_3hidpa was used in the synthesis of **4** and the crystal structure shows that carbon C(28) is in the *R* configuration and C(25) is in the *S* configuration. However, the complex crystallises in the non-centrosymmetric space group *Pbca*, but possesses glide planes and hence the enantiomer is present in the crystal lattice. The nitrogen is considered to be protonated from the interatomic O(4) · · · N distance [2.86(2) Å] which gives evidence of hydrogen bonding and the presence of a weak peak in the final difference map which gave a bond length and angles around the nitrogen corresponding to the presence of a proton. No protons are found on the carboxylic oxygen atoms, therefore, idpa is considered to have a charge of 2− and with one $[PPh_4]^+$ counter ion the metal is assigned to be Re^V. The bond length of Re=O(1) [1.66(1) Å] is comparable to that observed for **1** [Re=O(2) 1.666(7) Å, Table 2] and those for other $Re{=}O_{oxo}$ bonds reported.[20–24] There is no obvious *trans* weakening effect, as both the Re–O(2) and Re–O(3) bond lengths are essentially equivalent [2.05(1) and 2.02(1) Å]. This lack of *trans* lengthening is consistent with the observations of Mazzi and coworkers[21] for *trans*-$[ReOBr_2(PPh_3)L^4]$ and with the $5d^2$ electrons for Re^V being in the essentially non-bonding, 'in-plane' d_{xy} orbital. Binding of the ligand to the rhenium has occurred with the formal exchange of the hydroxyl group for a proton on the nitrogen atom in H_3hidpa giving the protonated 2,2′-iminodipropionate ligand. The binding of $idpa^{2-}$ involves chelate rings formed by ReO(2)C(29)C(28)N and ReO(3)C(26)C(25)N, with bite angles of O(2)–Re–N 75.0(5) and O(3)–Re–N 81.1(5)°. The Re–N bond length, 2.17(1) Å, is significantly longer than the Re–O(2) 2.05(1) and Re–O(3) 2.02(1) Å and this is a well documented feature of *O*,*N*,*O* or *O*,*N* donor ligands binding to ReO^{3+} centres.[20,23,25,38] The O–Re–N bite angle and Re–O and Re–N bond distances of the chelating ligand are similar to those observed in the complex $Ba_2[Re_2(\mu\text{-}O)_2(edta)_2]\cdot 4.5H_2O$[39] ($H_4$edta = ethylenedinitrilotetraacetic acid) where the bite angle for O–Re–N in the five-membered chelate is 76.8(2)°, Re–N is 2.198(6) Å and Re–O is 2.025(5) Å.

The green complex anion of complex **4** is six-co-ordinate with Re^V in a distorted octahedral geometry. The complex prepared from $[ReOCl_2(OEt)(PPh_3)_2]$ has retained the two chlorine atoms and the oxo group. The $hidpa^{3-}$ ligand has lost the hydroxyl group on the nitrogen atom, becoming $idpa^{2-}$, binding to the metal through two unidentate carboxylate oxygen atoms and the nitrogen atom. The IR spectrum showed two asymmetric modes for $\nu_{C=O}$ at 1701 and 1649 cm^{-1}; this correlates with the IR spectra reported[26] for the bonding of oxalic acid where two asymmetric $\nu_{C=O}$ are observed with a splitting of *ca.* 50 cm^{-1}. The ν_{C-O} is assigned at 1385 cm^{-1}, $\nu_{Re=O}$ at 980 cm^{-1} and ν_{Re-O} at 316 cm^{-1}, which correlate with the equivalent bands observed in the IR spectra of **1** and **2**. The negative-ion FAB mass spectrum of **4** showed the parent ion at *m/z* 432 with the appropriate isotopic splitting pattern.

Ligand fragments

The ligand fragments 2-oxidoiminopropionic acid, 2-iminopropionate and 2-[(1-carboxyethoxy)imino]propionic acid (Fig. 2) in compounds **3**, **2** and **1**, respectively, unlike the situation for the $[M(hidpa)_2]^{n-}$ (M = V, *n* = 1 or 2; M = Mo, *n* = 1) complexes[3,6] form no η^2-NO bonds, but bind to the metal through the nitrogen and one unidentate carboxylate oxygen atom. The ligand fragments in all three complexes form chelating rings consisting of a nitrogen doubly bonded to a carbon, a second carbon and an oxygen. Purified H_3hidpa was used in the reaction yielding **3**, which was obtained in good (*ca.* 40%) yields. Thus, the 2-oxidoiminopropionic acid ligand can be regarded as a derivative of the parent H_3hidpa ligand. A double bond has formed between the nitrogen and carbon [C(49)] with the loss of the second propionic acid group from the nitrogen (Fig. 4). 2-Oxidoiminopropionic acid has previously been synthesized by the condensation of sodium pyruvate with hydroxylamine[40] and has been complexed with various metal-(II) and -(III) metal centres (M = Co^{III}, Rh^{III}, Ir^{III}, Ru^{III}, Ni^{II}, Cu^{II} or Zn^{II})[41] and shows the same chelating ring structure.

The two rhenium complexes **1** and **2** were synthesized using unpurified H_3hidpa. Hence there is uncertainty as to whether the ligand fragments have been formed from the degradation of the H_3hidpa pro-ligand or whether these ligands already existed within the crude ligand syrup. For the reaction of $[ReOCl_3(PPh_3)_2]$ with the crude ligand syrup halide exchange had occurred with the chloro groups being replaced by bromo groups from either the ligand syrup or the $[PPh_4]$Br counter ion. However comparison with the molybdenum system suggests that rearrangement has occurred subsequent to the reaction with the rhenium complex. The ligand 2-[(1-carboxyethoxy)imino]propionic acid differs noticeably from H_3hidpa. As in the 2-oxidoiminopropionic acid a double bond has formed between the nitrogen and carbon [C(25)]. The second propionic acid group has migrated from being bound to the nitrogen onto the oxygen [O(6)] forming a new oxygen–carbon bond to the asymmetric carbon [C(28)] (Fig. 1). A search of Chemical Abstracts showed that 2-[(1-carboxyethoxy)imino]propionic acid is previously unreported as either a ligand or as an organic moiety. The ligand 2-iminopropionate shows only the chelating ring as observed in the two previous complexes. Complexation to the metal has occurred with formation of a double bond between the nitrogen and carbon [C(26)] with the loss of both a propionic acid and the hydroxyl group from the nitrogen (Fig. 3). 2-Iminopropionate has previously been reported[28] complexed to cobalt and shows the same chelate-type structure. In this case the ligand was formed *via* a template reaction between sodium pyruvate and $[Co(NH_3)_5(OH)]^{2+}$. This group also report that[28] the metal ion makes the imine NH group highly acidic, the N-protonated form being gained only on acidification. The formation of the nitrogen–carbon double bond in three of these ligands in the novel complexes results in the loss of a proton on the carbon and therefore the loss of at least one chiral centre in these molecules.

Conclusion

Two new rhenium compounds **1** and **2**, involving N,O-donor ligands, have been obtained following the reaction of $[PPh_4][ReOBr_4]$ or $[ReOCl_3(PPh_3)_2]$ with crude H_3hidpa, a product which had been previously used in reactions with $[VO(acac)_2]$[3] and $[MoO_2(acac)_2]$[7] to yield $[V(R,S\text{-hidpa})_2]^{2-/-}$ and $[Mo(R,S\text{-hidpa})(R,R\text{-hidpa})]^-$, respectively. A search of Chemical Abstracts has shown that 2-[(1-carboxyethoxy)imino]propionic acid is previously unreported, either as a ligand or as an organic moiety.

Reactions of H_3hidpa, purified by complexation with Zn^{2+} and subsequent acidic ion-exchange chromatography, with $[ReOCl_2(OEt)(PPh_3)_2]$ and $[PPh_4][MoOCl_4(H_2O)]$ yielded the products $[PPh_4][ReOCl_2(R,S\text{-idpa})]$ and $[PPh_4][MoO_2Cl_2(C_3H_4NO_3)]$, respectively. The salt $[PPh_4][ReOCl_2(R,S\text{-idpa})]$ showed the replacement of the hydroxyl group with a proton and retention of the two chloride atoms whilst $[PPh_4][MoO_2Cl_2(C_3H_4NO_3)]$ demonstrated the presence of a fragmentation product of the parent H_3hidpa ligand and the retention of two chlorides. The relatively high yields of these two products (*ca.* 60 and 40%, respectively) show that the complexation of the fragmented ligand product is significantly preferred to the binding of the hidpa^{3-} ligand of which no evidence was observed in the final products. Thus, it appears that these two organic moieties arise from the rearrangement and/or fragmentation of the *N*-hydroxy-2,2′-iminodipropionic acid under the influence of the metal–halogen centre. The reactions of the two rhenium compounds with the unpurified H_3hidpa ligand syrup have emphasised the importance of ligand purity if the chemistry of this pro-ligand was to be extended to metals other than vanadium, where the selectivity of the ligand for the metal is unlikely to be as high. Secondly, the reactions of the purified pro-ligand with $[ReOCl_2(OEt)(PPh_3)_2]$ and $[MoOCl_4(H_2O)]^-$ have emphasised the stability of the oxohalogenometal centre to substitution by hidpa^{3-}. This is noticeable particularly for the reaction of the purified H_3hidpa with $[MoOCl_4(H_2O)]^-$ where previously the $[Mo(hidpa)_2]^-$ complex has been synthesized from the reaction of $[MoO_2(acac)_2]$ with the crude pro-ligand. Thus, there appears to be an importance attached to the use of O-donor ligands in the metal-containing starting material. These considerations of ligand purity and metal starting material have now been used in the extension of the chemistry of H_3hidpa and its analogue H_3hida (*N*-hydroxyiminodiacetic acid) to the Group 4[42] and other Group 5[5] metals.

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