Oxygen Abstraction Reactions of N-Substituted Hydroxamic Acids with Molybdenum(V) and Vanadium(III) and -(IV) Compounds

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A wide range of **N-**substituted mono- and dihydroxamic acids undergo oxygen abstraction on reaction with V(III), V(IV), and Mo(V) compounds to form hydroxamates of V(V) and Mo(VI) respectively together with the corresponding amides and diamides. The molybdenyl and vanadyl hydroxamates form metal−oxygen clusters under FABMS conditions. The X-ray crystal structures of $[MoO_2\{CH_3(CH_2)_nC(O)N(C_6H_5)O\}_2$ (**1** and **2**) ($n = 4, 5$) show monomeric structures with structural trans effects and consequent weakening of the Mo−O(ligand) bonds which may account for the tendency to form clusters in FABMS. In constrast, the electrospray MS of the vanadyl dihydroxamates, $VO(OH)[PhN(O)C(O)(CH_2)_nC(O)N(O)Ph]$ ($n = 3, 5$) and $VO(OH)[p\text{-}CH_3C_6H_4N(O)C(O)\,(CH_2)_nC(O)N(O)C_6H_4\text{-}CH_3)$ ($n = 2, 4$) show the presence of dimers in solution.

Introduction

Hydroxamic acids are important bioligands.[1] Naturally occurring hydroxamic acids (siderophores) are involved in the microbial transport of iron and consequently have therapeutic uses in iron-related conditions.[2] They are also inhibitors of urease activity[3] and have been used therapeutically in the treatment of hepatic coma.[4] Their biological activity is related to their ability to form very stable chelates with a range of metals and most especially with iron.[5] In the majority of metal chelates formed by hydroxamic acids, coordination occurs by deprotonation of the OH group and subsequent O,O coordination of the carbonyl oxygen and deprotonated OH as in, for example $Fe(PhCONHO)_3$.[6] Although this mode of bonding has been confirmed by X-ray crystallography in a wide range of metal complexes, no examples have yet been observed of N,O coordination by normal hydroxamic acids which would involve deprotonation of the NH group despite recent experimental and theoretical studies[7,8] which, at least for RCONHOH, R = H, CH_3 suggest that these monohydroxamic acids are *N*-acids in the gas phase. However, aminohydroxamic acids such as glycinehydroxamic acid (GHA), $NH_2CH_2CONHOH$, provided the first example of N,N-coordination in $[(Ni(NH_2CH_2CONHO)_2]$,[9] and subsequent examples include the GHA complexes of Co(III)[10] and Cu (II).[11] There is now good evidence for a number of aminohydroxamic acids showing different coordination behavior, that is (N,N), (N,O), and (O,O), depending on the metal being complexed and on the pH of solution.[12]

In most cases of metal complexation by hydroxamic acids (HA), redox reactions do not occur and there is no change in oxidation number of the metal. In contrast, hydroxamates of V(IV), V(V), Mo(V), and Mo(VI) are well established[13] and their spectroscopic properties are consistent with O,O coordination by the hydroxamate ligands although relatively few X-ray crystallographic studies have been reported. Recently the crystal structures of oxochlorobis(benzohydroxamate)vanadium(V) and oxoisopropoxy(*N*,*N*′-dihydroxy-*N*,*N*-düsopropylheptanediamido)vanadium(V) were both shown to involve hydroxamate, O,O, coordination to vanadium.[14] To the best of our knowledge, the only analogous molybdenum structures are those of the hydroxamic acids (HA) derived from two analgesics, phenacetin and acetanilide, MoO_2A_2. In both cases the ligand arrangement about the Mo atom is distorted octahedral with the dioxo oxygens bonded *cis* to each other.[15]

However, in many cases, attempts to prepare V(IV) or Mo(V) hydroxamates from appropriate starting materials such as $VOSO_4{\cdot}xH_2O$ and $[NH_4]_2[MoOCl_5]$ give hydroxamates of the metals in higher oxidation states, i.e., $VO(OH)A_2$ and MoO_2A_2 (where HA = hydroxamic acid) and this has been generally attributed to the ease of oxidation of the hydroxamates of the metal in lower oxidation states.[13] Analogous uranyl hydroxamates are generally prepared from uranyl salts, e.g. $[U^{VI}O_2(NO_3)_2]$ and so metal oxidation is not observed on complexation

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(1) Kehl, H., Ed. *Chemistry and Biology of Hydroxamic Acids*; S. Karger: New York, 1982.

(2) Brown, D. A.; Chidambaram, M. V. In Metal Ions in Biological Systems; Sigel, H., Ed.; Marcel Dekker Inc.: New York, 1982; Vol. 14.

(3) Hase, J.; Kobashi, K. J. *Biochemistry (Tokyo)* **1967**, *62*, 293.

(4) Fishbein, W. N.; Strecter, C. L.; Daly, J. E. *J. Pharmacol. Exp. Ther.* **1973**, *186*, 173.

(5) Nielands, J. B. *J. Am. Chem. Soc.* **1952**, *74*, 4846.

(6) Lindner, V. H. J.; Gottlicher, S *Acta Crystallogr., Sect. B* **1969**, *25*, 632.

(7) Decouzon, M.; Exner, O.; Gal. J. F.; Nana, P. C. *J. Org. Chem.* **1990**, *55*, 3980.

(8) Ventura, O. N.; Rama, J. R.; Turi, L.; Dannenberg, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 5754.

(9) Brown, D. A.; Roche, A. L.; Pakkanen, T. A.; Pakkanen, T. K.; Smolander, K. *J. Chem. Soc., Chem. Commun.* **1982**, 676.

(10) Pakkanen, T. K.; Pakkanen, T. A.; Smolander, K.; Brown, D. A.; Glass, W. K.; Roche, A. L. *J. Mol. Struct.* **1987**, *162*, 313.

(11) De Miranda-Pinto, C. O. B.; Paniago, E. B.; Carvalho, S.; Tabak, M.; Mascarenhas, Y. P. *Inorg. Chem. Acta* **1987**, *137*, 145.

(12) Farkas, E.; Brown, D. A.; Cittaro, R.; Glass W. K. *J. Chem. Soc., Dalton Trans.* **1993**, 2803.

(13) Chatterjee, B. *Coord. Chem. Rev.* **1978**, *26*, 281.

(14) Fisher, D. C.; Barclay-Peet, S. J.; Balfe, C. A.; Raymond, K. N. *Inorg. Chem.* **1989**, *28*, 4399.

(15) Brewer, G. A.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 1823.

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with hydroxamic acids.[16] However, in one noteworthy case involving the reaction of uranium tetrachloride with the anion of *N*-phenylbenzohydroxamic acid (PBHA) in THF as solvent resulted in oxidation of U(IV) to U(VI) and formation of $UO_2Cl(PBA)(THF)_2$ accompanied by oxygen abstraction from some of the PBHA to form benzanilide.[17]

In the present paper, it will be shown that formation of hydroxamates of vanadium and molybdenum in higher oxidation states than the starter compounds occurs even under anaerobic conditions for a wide range of N-substituted mono and dihydroxamic acids and is accompanied by oxygen abstraction from the hydroxamic acid with formation of the corresponding amide, a reaction which has hitherto been unrecognized except in the case of U(IV) mentioned above.[17]

Results and Discussion

(A) Molybdenum Hydroxamates. Reaction of a series of *N*-arylmonohydroxamic acids (HA), $CH_3(CH_2)_nC(O)N(R)OH$ ($R = C_6H_5$, $n = 4, 5, 6, 8$; $R = p\text{-}CH_3C_6H_4$, $n = 5$) and *N,N′*-disubstituted dihydroxamic acids (H_2A'), $HON(R')C(O)(CH_2)_nC(O)N(R')OH$ ($R' = C_6H_5$, $n = 2, 3, 5, 7$; $R' = p\text{-}CH_3C_6H_4$, $n = 2, 3, 4, 7$; and $R' = p\text{-}C_2H_5C_6H_4$, $n = 5$) with both the molybdenum(V) reagent $(NH_4)_2[MoOCl_5]$ (method A) and the molybdenum(VI) reagent $Na_2MoO_42H_2O$ (method B) gave the corresponding molybdenyl, Mo(VI), hydroxamates, $Mo^{VI}O_2A_2$ and $Mo^{VI}O_2A'$, respectively. Formation of the Mo(VI) complexes thus occurs irrespective of the oxidation state (V or VI) of the molybdenum in the starting materials.

The two series of complexes obtained by methods A and B were shown to be identical by comparison of their microanalytical and infrared and ^1H NMR spectral data (see Supporting Information). The carbonyl infrared stretching frequencies which occur around 1590−1640 cm^{-1} in the free ligands occur in the complexes at about 1540 cm^{-1}, consistent with coordination of the carbonyl oxygen atom to the metal which, taken in conjunction with the disappearance of the OH band of the free ligand on complexation, supports O,O coordination for the hydroxamate ligand, and the appearance of a strong doublet in the 900−930 cm^{-1} region indicates a *cis*-MoO_2 group in all cases (Supporting Information).

FABMS. Satisfactory FABMS could only be obtained for $[MoO_2\{CH_3(CH_2)_nC(O)N(C_6H_5)O\}_2]$, $n = 4$ and 5, and $[MoO_2\{O(R)N(O)C(CH_2)_nC(O)N(R)O\}]$, $R = C_6H_5$, $n = 3$ and 7. As for the analogous uranyl complexes,[16] a series of oligomers of formula $[(MoO_2)_n]^+$ and $[(MoO_2)_nO_n]^+$ occur with clusters containing up to nine molybdenum atoms. The occurrence of oligomeric ions retaining a coordinated hydroxamate ligand is much rarer than that of the metal−oxygen clusters. Selected cluster peaks are given in the Supporting Information.

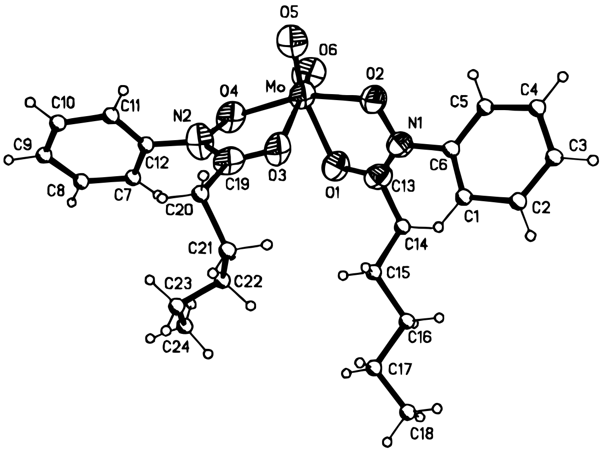

Figure 1. X-ray crystal structure of $MoO_2[CH_3(CH_2)_4C(O)N(O)C_6H_5]_2$ (**1**).

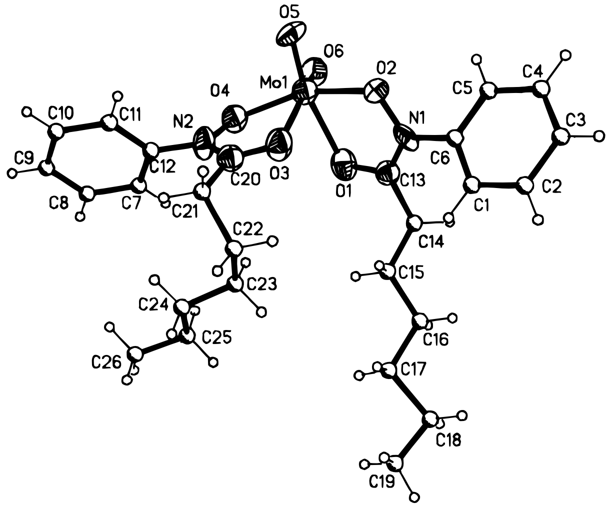

Figure 2. X-ray crystal structure of $MoO_2[CH_3(CH_2)_5C(O)N(O)C_6H_5]_2$ (**2**).

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{24}H_{32}MoN_2O_6$	$C_{26}H_{36}MoN_2O_6$
mol wt	540.5	568.5
cryst size, mm	0.7 × 0.2 × 0.1	0.5 × 0.3 × 0.1
space group (No.)	$P2_1/c$ (14)	*Pbca* (61)
a, Å	15.616(7)	10.406(6)
b, Å	10.408(4)	16.611(6)
c, Å	16.613(8)	33.027(7)
α, deg		
β, deg	100.69(4)	
γ, deg		
V, $Å^3$	2653(2)	5709(4)
Z	4	8
D_{calc}, g/cm^3	1.353	1.323
F(000)	1120	2368
μ, mm^{-1}	0.532	0.484
transm coeff	0.184/0.428	0.221/0.227
R, R_w[a]	0.111, 0.099	0.077, 0.049

[a] For all structures Mo Kα radiation was used at $T = 294$ K. SHELXTL-Plus: $1/w = \sigma^2(F) + 0.0001F^2$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

X-ray Crystal Structures. The crystal structures of the two molybdenyl monohydroxamates $[MoO_2\{CH_3(CH_2)_nC(O)N(C_6H_5)O\}_2]$ (**1** and **2**) ($n = 4$ and 5) are shown in Figures 1 and 2. Selected bond distances and angles are given in Tables 2 and 3 for **1** and in Tables 5 and 6 for **2** with crystallographic data in Table 1. They confirm the O,O mode of coordination of the hydroxamate ligands and cis-arrangement of the MoO_2 grouping as concluded from the spectroscopic data. The widespread occurrence of the *cis*-MoO_2 arrangement is in accord with extended Hückel calculations by Tatsumi and Hoffmann[18] and arises primarily from the maximum utilization of vacant "d" orbitals in π-bonding with oxygen lone pairs in the cis case. Clearly both complexes are monomeric so cluster formation in FABMS must arise under the conditions of the method. In both **1** and **2**, the molybdenum atoms lie in a distorted octahedral environment similar to those in the molybdenum complexes of phenacetin and acetanilide.[15] Thus the Mo−O(ligand) bonds *trans* to the terminal Mo−O bonds are elongated compared to the cis M−O(ligand) bonds, e.g. in **1**, n = 4, trans-Mo-O(ligand) = 2.19Å, which compares closely with those in ref 15; e.g.

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(16) Brown, D. A.; Ismail, S. *Inorg. Chem. Acta* **1990**, *171*, 41.
(17) Raymond, K. N.; Smith, R. L. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1431.
(18) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656.

Table 2. Selected Bond Lengths (Å) for **1**

Mo−O(1)	2.191(7)	Mo−O(2)	2.019(8)
Mo−O(3)	2.163(8)	Mo−O(4)	1.998(9)
Mo−O(5)	1.651(7)	Mo−O(6)	1.725(9)
O(1)−C(13)	1.254(16)	O(2)−N(1)	1.350(12)
O(3)−C(19)	1.233(17)	O(4)−N(2)	1.387(14)
N(1)−C(6)	1.465(16)	N(1)−C(13)	1.310(15)
N(2)−C(12)	1.408(18)	N(2)−C(19)	1.382(17)
C(13)−C(14)	1.532(16)	C(19)−C(20)	1.461(20)

Table 3. Selected Bond Angles (deg) for **1**

O(1)−Mo−O(2)	72.8(3)	O(1)−Mo−O(3)	77.7(3)
O(2)−Mo−O(3)	84.7(3)	O(1)−Mo−O(4)	94.0(3)
O(2)−Mo−O(4)	156.6(3)	O(3)−Mo−O(4)	73.4(3)
O(1)−Mo−O(5)	158.6(3)	O(2)−Mo−O(5)	87.0(3)
O(3)−Mo−O(5)	93.6(3)	O(4)−Mo−O(5)	102.3(4)
O(1)−Mo−O(6)	89.0(3)	O(2)−Mo−O(6)	109.1(4)
O(3)−Mo−O(6)	157.3(3)	O(4)−Mo−O(6)	89.5(4)
O(5)−Mo−O(6)	104.8(4)	Mo−O(1)−C(13)	114.6(7)
Mo−O(2)−N(1)	117.6(6)	Mo−O(3)−C(19)	116.5(8)
Mo−O(4)−N(2)	117.4(7)	O(2)−N(1)−C(6)	114.4(8)
O(2)−N(1)−C(13)	116.5(10)	C(6)−N(1)−C(13)	129.1(10)
O(4)−N(2)−C(12)	118.1(10)	O(4)−N(2)−C(19)	113.2(10)
C(12)−N(2)−C(19)	128.7(11)	O(1)−C(13)−N(1)	117.9(10)
O(1)−C(13)−C(14)	119.4(10)	N(1)−C(13)−C(14)	122.5(11)
O(3)−C(19)−N(2)	116.7(11)	O(3)−C(19)−C(20)	123.8(12)
N(2)−C(19)−C(20)	119.4(12)		

trans-Mo−O(average) = 2.20 Å over cis-Mo−O(average) 2.02 Å. This structural trans effect may lead to ready cleavage of the Mo−O(ligand) bond trans to the Mo═O terminal, thereby aiding the formation of molybdenum−oxygen bridges and hence clusters in the FABMS of these complexes:

$$MoO_2L_2 \rightarrow MoO_2L^+ + L$$

$$MoO_2L_2 + MoO_2L^+ \rightarrow Mo_2O_4L_3^{\;+}$$

Ion-neutral molecule reactions have been suggested previously as an explanation for the formation of clusters in the FABMS of related complexes.[19,20]

Oxygen Abstraction Reactions. In view of the previous report by Raymond and co-workers on the formation of a uranyl hydroxamate and benzanilide from the reaction of UCl_4 and *N*-phenylbenzohydroxamate,[17] we reinvestigated the above reactions with $(NH_4)_2[MoOCl_5]$ as starter under anaerobic conditions when both the Mo^{VI} hydroxamate and the corresponding amide or diamide formed; the latter were fully characterized by microanalysis, infrared and ^1H NMR spectroscopy, and EIMS (Supporting Information). Oxygen abstraction thus occurs from the hydroxamic acid to form the corresponding amide with concomitant oxidation of Mo(V) to Mo(VI) and formation of the molybdenyl complexes MoO_2A_2 and MoO_2A' (see Scheme 1). In a few cases, on addition of the ligand (in a water/methanol mixture) to $(NH_4)_2[MoOCl_5]$, it was noted that the initial orange/yellow color turned a deeper shade of orange which may be due to initial formation to the Mo^V hydroxamate prior to oxygen transfer occurring.

Scheme 1

$$(NH_4)_2[Mo^VOCl_5] + 3CH_3(CH_2)_nC(O)N(Ph)OH \rightarrow$$
$$Mo^{VI}O_2[CH_3(CH_2)_nCONPhO]_2 + CH_3(CH_2)_nC(O)N(Ph)H$$

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **1**

	x	*y*	*z*	*U*(eq)[a]
Mo	6408(1)	1948(1)	5137(1)	47(1)
O(1)	7478(4)	2761(8)	6033(5)	57(3)
O(2)	5895(4)	3336(8)	5751(5)	52(3)
O(3)	6373(5)	794(8)	6213(5)	53(3)
O(4)	7048(5)	324(8)	4999(5)	55(3)
O(5)	5399(5)	1582(8)	4705(5)	57(3)
O(6)	6850(5)	2643(9)	4365(4)	65(3)
N(1)	6422(6)	3892(10)	6392(6)	46(4)
N(2)	6943(6)	−698(10)	5508(7)	59(4)
C(1)	6140(8)	4631(13)	7729(7)	57(5)
C(2)	5712(9)	5503(14)	8174(8)	65(5)
C(3)	5140(8)	6359(14)	7776(8)	61(5)
C(4)	4949(7)	6416(13)	6920(8)	60(5)
C(5)	5392(7)	5580(12)	6495(7)	50(5)
C(6)	5977(7)	4755(11)	6876(7)	41(4)
C(7)	8079(9)	−2180(14)	5378(9)	73(6)
C(8)	8307(10)	−3426(18)	5181(11)	91(8)
C(9)	7694(12)	−4335(15)	4924(9)	77(7)
C(10)	6856(11)	−4023(16)	4847(9)	72(6)
C(11)	6569(8)	−2801(14)	5016(7)	55(5)
C(12)	7188(8)	−1931(13)	5286(7)	49(4)
C(13)	7251(8)	3599(12)	6493(7)	49(5)
C(14)	7929(7)	4146(14)	7196(8)	60(5)
C(15)	8249(8)	3127(17)	7842(8)	79(6)
C(16)	8746(10)	3791(20)	8644(10)	101(8)
C(17)	9066(13)	2675(29)	9272(13)	159(14)
C(18)	9401(16)	3294(30)	10037(19)	218(21)
C(19)	6604(8)	−336(14)	6185(7)	51(5)
C(20)	6512(8)	−1295(14)	6806(9)	70(6)
C(21)	7017(12)	−894(19)	7638(9)	100(8)
C(22)	8005(15)	−803(25)	7680(12)	134(12)
C(23)	8451(26)	−1900(32)	7824(20)	271(31)
C(24)	9377(20)	−1512(39)	7801(27)	406(37)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Lengths (Å) for **2**

Mo(1)−O(1)	2.206(9)	Mo(1)−O(2)	2.002(9)
Mo(1)−O(3)	2.163(9)	Mo(1)−O(4)	2.006(9)
Mo(1)−O(5)	1.699(9)	Mo(1)−O(6)	1.693(9)
O(1)−C(13)	1.267(17)	O(2)−N(1)	1.388(15)
O(3)−C(20)	1.244(17)	O(4)−N(2)	1.377(14)
N(1)−C(6)	1.425(14)	N(1)−C(13)	1.290(21)
N(2)−C(12)	1.400(13)	N(2)−C(20)	1.323(18)
C(13)−C(14)	1.516(21)	C(20)−C(21)	1.525(19)

Table 6. Selected Bond Angles (deg) for **2**

O(1)−Mo(1)−O(2)	73.5(4)	O(1)−Mo(1)−O(3)	77.6(4)
O(2)−Mo(1)−O(3)	83.9(3)	O(1)−Mo(1)−O(4)	93.0(3)
O(2)−Mo(1)−O(4)	156.5(3)	O(3)−Mo(1)−O(4)	74.3(3)
O(1)−Mo(1)−O(5)	157.5(3)	O(2)−Mo(1)−O(5)	85.3(4)
O(3)−Mo(1)−O(5)	93.1(4)	O(4)−Mo(1)−O(5)	104.2(4)
O(1)−Mo(1)−O(6)	88.7(4)	O(2)−Mo(1)−O(6)	109.0(4)
O(3)−Mo(1)−O(6)	157.9(4)	O(4)−Mo(1)−O(6)	89.4(4)
O(5)−Mo(1)−O(6)	105.6(4)	Mo(1)−O(1)−C(13)	113.8(9)
Mo(1)−O(2)−N(1)	117.0(8)	Mo(1)−O(3)−C(20)	113.2(8)
Mo(1)−O(4)−N(2)	115.5(7)	O(2)−N(1)−C(6)	114.1(11)
O(2)−N(1)−C(13)	116.9(11)	O(6)−N(1)−C(13)	129.0(11)
O(4)−N(2)−C(12)	116.9(9)	O(4)−N(2)−C(20)	114.6(10)
C(12)−N(2)−C(20)	128.4(11)	O(1)−C(13)−N(1)	118.4(13)
O(1)−C(13)−C(14)	117.4(13)	N(1)−C(13)−C(14)	124.2(13)
O(3)−C(20)−N(2)	119.7(13)	O(3)−C(20)−C(21)	118.6(12)
N(2)−C(20)−C(21)	121.7(12)		

Vanadium Complexes. Oxygen abstraction from hydroxamic acids (HA and H_2A') and formation of the corresponding amides and diamides also occurs with both V(III) and V(IV) compounds and concomitant formation of vanadium(V) hydroxamates, $V(O)(OH)(A)_2$, $V(O)OH(A')$, and, in a number of cases, $VOClA'$, e.g. $VOCl(O(R)N(O)C(CH_2)_nC(O)N(R)O)$ ($R = C_6H_5$, $n = 3$; $R = C_6H_4CH_3$, $n = 7$).

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(19) Ashton, P. R.; Fenton, D. E. *Inorg. Chem. Acta* **1988**, *146*, 99.
(20) Jennings, K. R.; Kemp, T. J.; Read, P. A. *Inorg. Chim. Acta* **1989**, *157*, 157.

Thus reaction of the above monohydroxamic and dihydroxamic acids with both the vanadium(IV) reagent $VO(SO_4)$ (method C), and the vanadium(V) reagent NH_4VO_3 (Method D) gave two identical series of complexes as confirmed by analysis, IR, NMR spectroscopy (Supporting Information). Similar structural arguments apply to the vanadium(V) complexes as to the above molybdenum(VI) series; for example in all cases the infrared spectra show a lowering of about 50 cm^{-1} of ν(CO) from the free ligand to the corresponding complex, disappearance of ν(OH) of the free ligand, and a sharp intense band at around 950−990 cm^{-1} assigned to the ν(V═O) stretching vibration consistent with *O*,*O*-hydroxamate coordination. Even when the reaction was carried out under anaerobic conditions, formation of the V^V complex occurred together with the appropriate mono or diamide, which again were fully characterized. The FABMS showed cluster formation of general formula $[(VO)_nO_m]^+$ containing up to 12 vanadium atoms being observed with the instrumentation available. The FABMS of $VO(OH)\{C_6H_5(O)N(O)C(CH_2)_4C(O)N(O)C_6H_5)\}$ and the assignments of the major cluster peaks are given in the Supporting Information. There was no evidence for retention of the V(OH) group in the clusters, suggesting that this group is very easily abstracted under FABMS conditions. Unfortunately, we were not able to obtain crystals suitable for X-ray crystal structural studies for any of the above series but known X-ray crystal structures, e.g. that of $VOCl(PhCONHO)_2$,[14] suggest that again cluster formation occurs by molecule−ion reactions in the FABMS experiments. A number of V(IV) primary hydroxamates have been prepared from $VOSO_4$[13] suggesting that N-substitution favors oxygen abstraction. It is hoped that mechanistic studies currently in progress[21] will clarify this point.

Reactions with VCl_3 (Method E). In this case, oxidation and oxygen abstraction again occurred on reaction with the above hydroxamic acids (in a 1:2 ratio of V/HA) but a number of the dihydroxamic acids (H_2A') gave the corresponding oxo−chloro complexes of V(V) as well as the corresponding diamides (Scheme 2).

Scheme 2. Methods C−E

Method C

$$V^{IV}SO_4{\cdot}xH_2O + 2H_2A' \xrightarrow[H_2O/acetone]{-2H^+N_2} V^VO(OH)A' + H(R)N(O)C(CH_2)_nC(O)N(R)H$$

Method D

$$NH_4V^VO_3 + H_2A' \xrightarrow[water/acetone]{-2H^+N_2} V^VO(OH)A'$$

Method E

$$VCl_3 + H_2A' \xrightarrow[water/acetone]{-2H^+N_2} V^VO(Cl)A' + H(R)N(O)C(CH_3)_nC(O)N(R)H$$

Schemes 1 and 2 both involve stoichiometric ratios of hydroxamic acid to starter metal compound of 3:1 as employed in this work; however, because of the difficult separation and extensive purification of the products required, resulting in yields of not more than 30%, it was not possible to verify the stoichiometry of the products. However, mechanistic studies in progress[21] have confirmed the stoichiometry in the case of the reaction between *N*-phenylhexanohydroxamic acid and VCl_3 in chloroform where yields of more than 80% have been obtained with the stoichiometry shown in Scheme 2, method E.

Dimerization of V(V) Dihydroxamates. Electrospray Spectra of $VO(OH)[C_6H_5N(O)\ C(O)(CH_2)_nC(O)N(O)C_6H_5]$ (n = 3, 5) (10a,b) and $VO(OH)[p\text{-}CH_3C_6H_4N(O)C(O)(CH_2)_nC(O)N(O)C_6H_4\text{-}p\text{-}Me)$ (n = 2, 4), (10c,d). Satisfactory NMR spectra could not be obtained for the dihydroxamate complexes of V(V) due to their poor solubility in a range of NMR solvents suggesting that they are dimeric in solution as observed in the crystal structure of $VO(OiC_3H_7)(ON(i\text{-}C_3H_7)C(O)(CH_2)_nC(O)N(i\text{-}C_3H_7)O)$ ($n = 5$) and also indicated from molecular weight measurements for $n = 3$. Only in the case of $n = 10$ was a monomer indicated.[14] The ready formation of metal clusters in FABMS above also means that parent ion peaks due to dimeric structures could not be identified thereby precluding this technique as a means of structure determination. However the electrospray mass spectra of the above series gave clear evidence for the occurrence of dimers in the four compounds, **10a**−**d**, (n = 3, 5, 2, 4), in methanol solution and provides a striking example of the advantages of this most gentle ionisation method.

Compound **10a**, $n = 3$ gave a spectrum with a strong peak at *m*/*z* 789 with fairly intense lines at 790−792 signifying additional protons, together with weaker peaks at 682, 586, 511 and some others. The peaks at 789−792 correspond to the dimeric formulation (where A′ = ligand dianion) $A'_2V_2O_4H_n{}^+$ ($m/z = 790 + n$), although why the peak corresponding to $n = -1$ is the most intense is unclear. The peak at *m*/*z* 682 corresponds to loss of PhNO from one ligand of the dimer, while that at *m*/*z* 586 refers to $(A'V_2O_4HPhNO)^+$ (m/z = 586). Chemically-induced decomposition of the ion of mass 790 gave daughter ions at m/z = 682 and 493; the latter is attributable to $(A'V_2O_5)^+$.

Compound **10c**, $n = 2$, gave a dominant peak at m/z = 817.24 attributed to the dimer $(A'V_2O_4)^+$ (m/z = 818). No vestige of the monomer ion was present. Compound **10d**, n = 4, gave a main peak at m/z = 873.26: the dimer $(A'V_2O_4)^+$ has m/z = 874 with high-mass satellites at 888.68 $(A'V_2O_5)^+$ and 905.34 $(A'V_2O_6)^+$. Compound **10b**, n = 5, gave a main peak at *m*/*z* 845.25 attributed to the dimer $(A'V_2O_4)^+$ (m/z = 846) and satellites at *m*/*z* 861 ($A'V_2O_5{}^+$ = 862) and 877 ($A'V_2O_6{}^+$ = 878). Collision-induced decomposition of the mass 845 ion gave a spectrum dominated by fragments at m/z = 738 (attributed to loss of PhNO) and 521 due possibly to $(A'V_2O_5)^+$ (m/z = 522); a smaller peak at m/z = 813 signifies loss of O_2 to give $(A'V_2O_2)^+$ (Supporting Information).

These results parallel quite closely those obtained recently by Crumbliss et al.[22] for the ESMS of 1:1 ferric dihydroxamates in acetonitrile/water mixtures where dimer peaks occurred for hydroxamic acids with $n = 2$ and 4, and only for the long chain acid ($n = 8$) did the corresponding monomer predominate. Clearly steric constraints in the shorter chain dihydroxamic acids results in dimer formation as illustrated by the crystal structure of $VO[i\text{-}C_3H_7N(O)C(O)(CH_2)_5C(O)N(O)\text{-}i\text{-}C_3H_7]$.[14]

Conclusions

Oxygen abstraction from N-substituted mono- and dihydroxamic acids by V(III), V(IV), and Mo(V) compounds and their concomitant oxidation to V(V) and Mo(VI) occurs for a range of hydroxamic acids. Reduction of hydroxamic acids to amides occurs with phosphines[23] and nitroso compounds[24] to form phosphine oxides and nitro compounds. In the former case an

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(21) Cittaro, R. Private communication.

(22) Caudle, M.; Stevens, R. D.; Crumbliss, A. L. *Inorg. Chem.* **1994**, *33*, 6111.

intramoleculear mechanism is indicated by double labeling experiments.[23]

Metal-centered oxygen atom transfer reactions have been comprehensively reviewed by Holm[25] with particular emphasis on molybdenum centered reactions where μ-oxo dimer formation often occurs. The detailed mechanism of the oxygen abstraction reaction reported in this paper is not clear but may involve prior formation of the lower valence state complex, e.g. Mo(IV), prior to oxygen abstraction from the hydroxamic acid and the observation of transient colors in some reactions with the Mo(IV) starter supports this idea. We have obtained no evidence so far for the formation of a μ-oxo-dimer. Further mechanistic studies are in progress.[21]

Experimental Section

Solvents were freshly dried by standard methods. Reagents were used directly. Reactions studied under anaerobic conditions used solvents which were degassed under N_2 and carried out under dry nitrogen using standard septum techniques. Infrared spectra were measured, either using a 0.1 mm CaF_2 cell or as a KBr disk on a Perkin Elmer 1720 FT spectrometer linked to a Model 3700 data station. ^1H and ^{13}C NMR spectra were recorded on a JEOL GX27O spectrometer. Analyses were performed by the Microanalytical Unit of the Chemical Services Unit of University College, Dublin. EI Mass Spectra were recorded on a Finnegan Matt Incos 50 mass spectrometer with an integrated FCMS system. FABMS were run in a glycerol matrix on a VG7OE mass spectrometer with argon as bombardment gas at 8 kV. ESMS were run on a Fisons "Quattro II" triple quadrupole mass spectrometer at the University of Warwick, U.K.

Preparation of Hydroxamic Acids. The *N*-phenyl and *N*-tolyl-substituted hydroxamic acids were prepared by reaction of *N*-phenyl- or *N*-tolylhydroxylamine with the appropriate acid (or diacid) chloride.[26]

Preparation of *N*-Arylhydroxylamines. These were prepared by a modified version of that reported by Brink and Crumbliss;[27] for example, 20 mL of nitrobenzene was added to a stirred solution of zinc dust in a 1:1 ethanol/water mixture (200 mL) followed by dropwise addition of saturated ammonium chloride until a temperature of 65 °C was reached and maintained for 3 h by intermittent cooling (NH_4Cl/ice bath). After filtration, addition of sodium chloride (150 g) and cooling in an ice bath gave the *N*-arylhydroxylamine which was separated from NaCl by addition of ether (75 mL), filtration and subsequent reduction of solvent volume to give light yellow crystals. In the case of *N*-phenylhydroxamine, prompt use is essential since the compound decomposes in air and light.

Preparation of Hydroxamic Acids. A typical preparation is given for *N*,*N*′-diphenylpimelohydroxamic acid, $HON(Ph)C(O)(CH_2)_5C(O)N(Ph)OH$.

To a suspension of freshly crystallized *N*-phenylhydroxylamine (19.8 g, 0.18 mmol) in 500 mL of ether was added a suspension of $NaHCO_3$(25.0 g, 0.3 mol) in water (40 mL) and the mixture cooled to −10 °C followed by dropwise addition of pimeloyl chloride (10.9 g, 0.06 mol) over 1 h with stirring. The product was filtered and saturated with a 10% solution of $NaHCO_3$, filtered, washed with cold water and recrystallized from hot acetone to give white needles of *N*,*N*′-diphenylpimelohydroxamic acid.

Preparation of Molybdenyl Hydroxamates $MoO_2(A)_2$ and $MoO_2(A')$ from the Corresponding Monohydroxamic Acid (HA) and Dihydroxamic Acids (H_2A'). Method A from the Mo(V) Reagent, $(NH_4)_2[MoOCl_5]$. A typical preparation is given for $MoO_2\{CH_3(CH_2)_4C(O)N(Ph)O\}_2$. $(NH_4)_2[MoOCl_5]$, was prepared by the method of Simon and Souchay.[28]

Table 7. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **2**

	x	*y*	*z*	*U*(eq)[a]
Mo(1)	1961(1)	4893(1)	653(1)	45(1)
O(1)	2765(8)	5617(6)	1152(3)	54(4)
O(2)	3319(8)	5595(5)	409(3)	50(4)
O(3)	806(8)	5975(5)	629(3)	57(4)
O(4)	350(9)	4639(5)	961(3)	48(4)
O(5)	1608(8)	4637(4)	167(3)	49(4)
O(6)	2666(8)	4070(5)	857(3)	54(4)
N(1)	3879(10)	6166(6)	659(4)	41(5)
N(2)	−649(10)	5171(7)	908(3)	50(5)
C(1)	4679(7)	7538(5)	534(2)	50(4)
C(2)	5520	8054	332	50(4)
C(3)	6392	7746	52	52(5)
C(4)	6425	6921	−27	48(4)
C(5)	5584	6405	175	44(4)
C(6)	4712	6713	456	39(4)
C(7)	−2143(8)	4838(5)	1444(2)	66(4)
C(8)	−3371	4611	1569	90(6)
C(9)	−4326	4461	1282	66(5)
C(10)	−4052	4539	870	58(5)
C(11)	−2823	4766	746	57(4)
C(12)	−1869	4916	1033	43(3)
C(13)	3580(14)	6136(9)	1038(5)	39(4)
C(14)	4127(13)	6695(8)	1358(4)	59(5)
C(15)	3134(14)	7318(8)	1503(4)	63(5)
C(16)	3719(15)	8001(9)	1752(5)	98(7)
C(17)	2644(15)	8585(9)	1900(5)	108(6)
C(18)	3415(19)	9311(11)	2124(7)	172(10)
C(19)	2273(22)	9808(12)	2230(7)	291(16)
C(20)	−316(14)	5870(9)	747(5)	44(4)
C(21)	−1286(12)	6549(7)	690(5)	63(5)
C(22)	−811(14)	7294(8)	942(4)	76(5)
C(23)	−675(16)	7220(10)	1391(5)	90(6)
C(24)	−1938(18)	7171(11)	1589(5)	118(7)
C(25)	−1695(22)	6985(13)	2077(7)	189(11)
C(26)	−2992(25)	6957(14)	2215(8)	340(20)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

To a warm deaerated aqueous solution (25 mL) of ammonium oxopentachloromolybdate (0.34 g, 1.9 mmol) was added under nitrogen a deaerated methanolic solution (25 mls) of *N*-phenylhexanohydroxamic acid (1.2 g, 5.7 mmol) and heated on a steam bath for 1 h whereupon the color changed from orange to a greenish/yellow. After refrigeration overnight, pale yellow crystals of $MoO_2\{CH_3(CH_2)_4CONPhO\}_2$ formed, which were dried over $CaCl_2$. The filtrate was reduced in volume and on cooling overnight deposited a gray powder which on recrystallization analyzed as $CH_3(CH_2)_4CONHPh$ (Supporting Information).

Method B from the Mo(VI) Reagent, $Na_2MoO_4\cdot 2H_2O$. An ethanolic solution (20 mL) of *N*-phenylhexanohydroxamic acid (0.42 g, 2 mmol) was added with stirring to an aqueous solution (20 mL) of sodium molybdate (0.19 g, 1 mmol) to give immediately a light yellow colored solution from which, after addition of 6 N HCl to adjust the pH to 3, yellow crystals precipitated. Recrystallization from hot ethanol gave shining yellow crystals (96% yield) suitable for X-ray analysis.

Preparation of Vanadium Hydroxamates $VO(OH)(A_2)$ and $VO(OH)(A')$. Method C from the V(IV) Reagent, $VOSO_4$. A hot deaerated aqueous solution (15 mL) of $VOSO_4$ (0.16 g, 1 mmol) was added dropwise under nitrogen to a hot acetone solution (15 mL) of *N*-phenylhexanohydroxamic acid (0.42 g, 2 mmol) and heated on a water bath for 30 min. When the mixture was cooled overnight, violet crystals of $VO(OH)\{CH_3(CH_2)_4CONPhO\}_2$ formed. Removal of solvent from the filtrate gave a gray powder which on recrystallization from $CHCl_3$ gave colorless crystals of $CH_3(CH_2)_4CONHPh$.

Method D from the V(V) Reagent, NH_4VO_3. A hot aqueous solution (20 mL) of ammonium vanadate (0.12 g, 1 mmol) was added dropwise with stirring to a solution of *N*-phenylhexanohydroxamic acid (0.42 g, 2 mmol) in acetone (20 mL). Adjusting the pH to 2.3 by addition of 2M H_2SO_4 and standing overnight at 3 °C gave a precipitate, which on washing and drying over $CaCl_2$ gave violet crystals of $VO(OH)\{CH_3(CH_2)_4CONPhO\}_2$.

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(23) Forrester, A. R.; Ogiling, M. M.; Thomson, R. H. *J. Chem. Soc. B* **1970**, 1081.
(24) Kurtzweil, M. L.; Loo, D.; Beak, P. *J. Am. Chem. Soc.* **1993**, *115*, 421.
(25) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.
(26) Gupta, V. K.; Tandon, S. J. *J. Ind. Chem. Soc.* **1969**, *46*, 9.
(27) Crumbliss, A. L.; Brink, C. P. *J. Org. Chem.* **1982**, *47*, 1171.
(28) Simon, J. P.; Souchay, P. *Bull. Soc. Chim. Fr.* **1956**, 1402.

Method E from the V(III) Reagent, VCl_3. VCl_3 gave in most cases the vanadium(V) $VO(OH)(A_2)$ and $VO(OH)(A')$ series; however, for $HONRCO(CH_2)_nCONROH$), where R = C_6H_5, $n = 3$, and R = $C_6H_4CH_3$, $n = 7$, the chloro complexes $VOCl(A')$ were obtained. For example, VCl_3 (0.16 g, 1 mmol) in dry deoxygenated acetone (15 mL) was added dropwise to a hot acetone solution (20 mL) of *N*,*N′*-diphenylglutarohydroxamic acid (0.32 g, 1 mmol). After the solution was refluxed for 45 min under N_2, a black precipitate of $VOCl[OPhNOC(CH_2)_3CONPhO]$ formed. Removal of solvent under vacuum from the filtrate gave a grayish powder which on recrystallization gave the diamide, $PhNHOC(CH_2)_3CONHPh$. Satisfactory analyses were obtained for all the above compounds (see Supporting Information).

Structure Determination of $[MoO_2\{CH_3(CH_2)_4C(O)N(C_6H_5)O\}_2]$ (1) and $[MoO_2\{CH_3(CH_2)_5C(O)N(C_6H_5)O\}]$ (2). Lattice parameters were refined from 32 (**1**) and 35 (**2**) reflections with $10° \le 2\theta \le 30°$. Data were collected at room temperature on a Siemens R3 m/V diffractometer, with ω-scan, $4 \le 2\theta \le 50°$ for **1** and $3 \le 2\theta \le 40°$ for **2**, 5355 (**1**) and 6207 (**2**) reflections measured, three check reflections recorded every 100, and 4% decay for **1** corrected. *Lp* and empirical absorption corrections were done (ψ scans). The structures were solved by direct methods and refined by full-matrix least-squares techniques (SHELXTL-Plus).[29] All non-hydrogen atoms except C24 for **1** and the carbon atoms in **2** were refined anisotropically; hydrogen atoms were refined in calculated positions (C−H = 0.96 Å) riding on the corresponding carbon atoms. The phenyl rings in **2** were refined as regular hexagons (C−C = 1.395 Å). The residuals in the final ΔF map were 1.6 (**1**) and 0.8 (**2**) e/Å^3 close to the Mo atoms. Scattering factors were taken from standard sources.[30] Further details are given in Tables 1, 4, and 7.

Electrospray Ionization Mass Spectrometry. The electrospray ionization−collision-induced decomposition (ESI/CID) experiments were carried out in a Fisons' "Quattro II" triple quadrupole mass spectrometer (VG Biotech, Altrincham, U.K.) equipped with an atmospheric pressure ionisation (API) source operated in the nebulizer-assisted electrospray mode. The potential on the electrospray needle was set at 3.6 kV, and the extraction cone voltage was normally set at 30V. Vanadium(V) hydroxamates at a concentration of 1.0 μg/μL were dissolved in methanol by sonication followed by removal of excess solid by centrifugation. Aliquots of 10 μL were introduced into the ion source at a flow rate of 5 μL/min. Mass spectra were acquired over the range *m*/*z* 1500 to *m*/*z* 80 during a 10 s scan, and by operating the data system in the multichannel acquisition (MCA) mode, several scans were summed to produce the final spectrum. Calibration was carried out using a solution of sodium iodide. Dimeric ions of selected *m*/*z* passed from the first quadrupole mass analyzer into the rf-only quadrupole collision cell containing argon at 3.8×10^{-3} mbar at a translation energy of 15 eV. Fragment ion spectra were obtained by scanning the final quadrupole mass analyser over the *m*/*z* range from the mass of the precursor ion down to *m*/*z* 40 in 10 s using the MCA mode.

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Supporting Information Available: Tables of analytical data for complexes, hydroxamic acids, and amides, infrared data, ^1H and ^{13}C NMR data, cluster peaks in selected FABMS, and the ESMS of compound **10a** in methanol, and figures showing the collision−induced decomposition spectra of $m/z = 845$ peak from the mass spectrum of $VO(OH)[O(C_6H_5)N(O)C(CH_2)_5C(O)N(C_6H_5)O]$ (34 pages). Ordering information is given on any current masthead page.

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(29) Sheldrick, G. M. SHELXTL-Plus. Siemens Analytical Instruments Inc., Madison, WI, 1991.

(30) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.