Molybdenum(VI) Peroxo α-Amino Acid Complexes: Synthesis, Spectra, and Properties of $MoO(O_2)_2$(α-aa)(H_2O) for α-aa = Glycine, Alanine, Proline, Valine, Leucine, Serine, Asparagine, Glutamine, and Glutamic Acid. X-ray Crystal Structures of the Glycine, Alanine, and Proline Compounds

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The compounds $MoO(O_2)_2$(α-aa)(H_2O), α-aa = glycine (**1**), alanine (**2**), proline (**3**), valine (**4**), leucine (**5**), serine (**6**), asparagine (**7**), glutamine (**8**), and glutamic acid (**9**), were prepared from the acidic aqueous solutions and characterized by examination of their IR, ^{1}H and ^{13}C NMR, and UV−visible spectra. They represent the first complexes containing a peroxo−α-amino acid combination in a metal ion ligand sphere. The synthesis and crystallization of these complexes was pH and concentration dependent, and their stability varied for different α-amino acids. X-ray structural studies of **1**−**3** have shown that the α-amino acids are coordinated as a zwitterion via one oxygen. This oxygen of the monodentate carboxylato group occupies an equatorial position in a distorted pentagonal bipyramid and encloses the pentagonal ring with the two bidentate peroxo groups. The apical positions are occupied by an oxo group and a water molecule, respectively. The Mo−O(O_2) bonds are nonsymmetrical, differing in length by 0.009−0.045 Å. The longer bonds are located next to the coordinated carboxylato oxygen. A correlation between O−O and Mo−O bond lengths with the IR and UV−visible spectra of complexes **1**−**3** is discussed. Crystal structure of $MoO(O_2)_2$(alanine)(H_2O): monoclinic, space group $P2_1/c$; $Z = 4$; $a = 10.727(3)$ Å; $b = 8.026(2)$ Å; $c = 10.794(4)$ Å; $\beta = 110.81(2)°$; $V = 869$ (Å)^3; $R = 0.041$. ^{1}H and ^{13}C NMR spectra in D_2O solutions showed the presence of one complex species, which decomposed by standing in solution. Analogies and differences between Mo(VI) and V(V) peroxo complexes are outlined.

Introduction

Peroxo complexes of Mo(VI) have been known for a long time,[1−3] and their catalytic activity has been a topic of considerable interest.[4−6] We have also observed the unusual catalytic conversion of malic and malonic acids to oxalates,[7] occurring in the molybdenum(VI) peroxide solutions. Studies of the reactivity of heteroligand Mo(VI) peroxo complexes in aqueous solutions have shown large differences in the lability of Mo(VI) peroxides containing different heteroligands.[8] Our studies of the Mo(VI) peroxo α-amino acid complexes have been undertaken in order to answer a few fundamental questions. First of all, do particular α-amino acids remain unchanged in the hydrogen peroxide solutions of molybdenum(VI), and if unchanged, do they coordinate to the metal ion along with the bidentate peroxo group(s)? Finally, within the coordination sphere of molybdenum, which are the donor atom(s), and what is then the molecular structure? Some time ago,[9] we published a preliminary report on the structure of $MoO(O)_2$(α-aa)(H_2O), α-aa = glycine, proline. In this paper we report syntheses, spectral data, and properties of the $MoO(O_2)_2$(α-aa)(H_2O) series, with the α-amino acids containing nonpolar R groups when α-aa = alanine (**2**), proline (**3**), valine (**4**), and leucine (**5**) and uncharged polar R groups when α-aa = glycine (**1**), serine (**6**), asparagine (**7**), glutamine (**8**), and glutamic acid (**9**) (in acidic solutions). The compounds were characterized in the solid state by examination of their IR, ^{1}H and ^{13}C NMR, and UV−visible spectra. X-ray structures of the glycine (**1**), alanine (**2**), and proline (**3**) complexes are presented.

Experimental Section

Materials. Reagent grade MoO_3, H_2O_2 (30%), glycine, alanine, proline, valine, leucine, serine, asparagine, glutamine, and glutamic acid were used. All solvents were reagent grade.

CAUTION! Peroxo molybdates in the presence of organic ligands and some solvents are potentially explosive. These complexes should be prepared only in small quantities, in a hood with a protective shield, and handled with care.

Preparation of $MoO(O_2)_2$(glycine)(H_2O) (1). MoO_3 (1.41 g, 10 mM) was dissolved in hydrogen peroxide (10 mL, 30%, 80 mM) with gentle stirring at 30−40 °C for 4−5 h. Glycine (0.75 g, 10 mM) was gradually added to the clear solution, and stirring was continued until all solid was dissolved. The solution was left standing, and after about 24 h the bright yellow crystals obtained were filtered off (pH of the

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solution ~3.8), washed with ethanol (95%), and dried over Drierite. Yield: ~35%. Anal. Calcd for $MoC_2H_7NO_8$: C, 8.9; H, 2.6; N, 5.2; O_2^{2-}, 23.8. Found: C, 8.9; H, 2.6; N, 5.1; O_2^{2-}, 23.8.

Preparation of $MoO(O_2)_2$(alanine)(H_2O) (2). MoO_3 (1.41 g, 10 mM) was dissolved in hydrogen peroxide as described for **1**, and alanine (0.90 g, 10 mM) dissolved in water (10 mL) was added gradually with constant stirring and gentle heating (50−60 °C) for about 3 h. The clear yellow solution was left standing overnight (or longer). A small portion of this solution was evaporated and the residue redissolved in hydrogen peroxide. Crystals obtained from this portion were used to seed the bulk of the solution (pH ca. 1.1), and the crystalline precipitate obtained was washed with ethanol (95%) and dried over Drierite. Yield: ~40%. Anal. Calcd for $MoC_3H_9NO_8$:C, 12.7; H, 3.2; N, 4.9; O_2^{2-}, 22.6. Found: C, 12.7; H, 3.2; N, 4.9; O_2^{2-}, 22.6.

Preparation of $MoO(O_2)_2$(proline)(H_2O) (3). MoO_3 (1.41 g, 10 mM) was dissolved in hydrogen peroxide as described for **1**, and proline (11.5 g, 10 mM) dissolved in water (10 mL) was added with stirring and heating (65−70 °C) for about 2 h. The reaction mixture was left standing for about 1−2 days, after which a yellow crystalline precipitate was obtained. The precipitate was washed (by decanting) with water (3−4 mL) and then alcohol (95%, 5−6 mL). Yield: ~40%. From the mother liquid (pH ca. 1.9), left standing longer, were obtained larger crystals. The compound is photosensitive and must be kept in a dark, dry atmosphere. Anal. Calcd for $MoC_5H_{11}NO_8$: C, 19.4; H, 3.6; N, 4.5; O_2^{2-}, 20.7. Found: C, 19.0; H, 3.7; N, 4.4; O_2^{2-}, 21.0.

Preparation of $MoO(O_2)_2$(valine)(H_2O) (4). MoO_3 (1.41 g, 10 mM) was dissolved in hydrogen peroxide as described for **1**, and valine (1.18 g, 10 mM) was added with stirring and gentle heating (30−40 °C). The clear solution was evaporated to 5−6 mL (pH ca. 1.1), and a crystalline yellow precipitate was obtained overnight, filtered, and washed with ether (the complex is slightly soluble in water and alcohol). Yield: ~55%. Anal. Calcd for $MoC_5H_{13}NO_8$: C, 19.3; H, 4.2; N, 4.5; O_2^{2-}, 20.5. Found: C, 19.5; H, 4.3; N, 4.5; O_2^{2-}, 20, 5.

Preparation of $MoO(O_2)_2$(leucine)(H_2O) (5). MoO_3 (2.85 g, 20 mM) was dissolved in hydrogen peroxide (30%, 10−15 mL, 80−120 mM) as described for **1**, and to the clear solution was added leucine (2.70 g, 20 mM), with stirring. The solution (pH ca. 1.2) was left standing. A polymeric mass with aggregates of hair-thin crystals was obtained, slightly soluble in alcohol. The precipitate was washed with ether and stored over Drierite. Anal. Calcd for $MoC_6H_{15}NO_8$: C, 22.2; H, 4.6; N, 4.3; O_2^{2-}, 19.7. Found: C, 20.7; H, 4.8; N, 4.3; O_2^{2-}, 19.8.

Preparation of $MoO(O_2)_2$(serine)(H_2O) (6). MoO_3 (2.85 g, 20 mM) was dissolved in hydrogen peroxide (30%, 10 mL, 80 mM), and solid serine (2.10 g, 20 mM) was added gradually with stirring, each portion being dissolved in turn. The clear orange-yellow solution (pH ca. 1.6) was stirred at room temperature for about 2 h and left evaporating at room temperature. A polymeric residue was obtained (soluble in water and hydrogen peroxide), washed with ether, and dried over Drierite. Anal. Calcd for $MoC_3H_9NO_9$: C, 12.0; H, 3.0; N, 4.7; O_2^{2-}, 21.4. Found: C, 11.2; H, 2.9; N, 4.7; O_2^{2-}, 19.6.

Preparation of $MoO(O_2)_2$(asparagine)(H_2O) (7). MoO_3 (1.45 g, 10 mM) was dissolved in hydrogen peroxide as described for **1**, and solid asparagine (1.33 g, 10 mM) was added to the clear solution and dissolved with stirring (at 30−40 °C). Overnight a yellow needle-like microcrystalline solid was obtained from the solution (pH ca. 1.8), soluble in water and DMSO, where it quickly decomposed in both. The precipitate was washed with ethanol (96%) and dried over Drierite. Crystals standing over Drierite were stable for months. Yield: ~60%. Anal. Calcd for $MoC_4H_{10}N_2O_9$: Mo, 29.4; C, 14.7: H, 3.09; N, 8.59; O_2^{2-}, 19.6. Found: Mo, 28.2; C, 14.7; H, 3.09; N, 8.5; O_2^{2-}, 18.7.

Preparation of $MoO(O_2)_2$(glutamine)(H_2O) (8). MoO_3 (1.43 g, 10 mM) was dissolved in hydrogen peroxide as described for **1**. Solid glutamine was added gradually with stirring, and the solution was heated (at 50 °C) for 4−5 h. A solid precipitated overnight from this solution (pH ca. 1.6). The solid was washed quickly by decanting with ethanol and dried on Drierite. Small amount of the complex was soluble in DMSO, but a slightly larger amount explosively decomposed and charred in contact with DMSO. The complex was easily soluble in water (glutamine is not), but the recrystallization of the solid from water/hydrogen peroxide solution yielded impure products. Anal. Calcd for $MoC_5H_{12}NO_9$: Mo, 28.2; C, 17.7; H, 3.6; N, 8.2; O_2^{2-}, 18.8. Found: Mo, 28.1; C, 17.6; H, 3.6; N, 8.2; O_2^{2-}, 17.0.

Preparation of $MoO(O_2)_2$(glutamic acid)(H_2O) (9). MoO_3(0.73 g, 5 mM) was dissolved in hydrogen peroxide (30%, 5 mL, 40 mM), solid glutamic acid (1.47 g, 10 mM) was added with stirring, and the reaction mixture was gently heated (35 °C) for 2−3 h. Excess glutamic acid was filtered off, and the clear solution was left standing (pH ca. 1.8). A viscous solid which precipitated after a few hours was washed with ethanol and dried on Drierite. It was slightly soluble in ethanol and DMSO, sometimes with vigorous decomposition. Anal. Calcd for $MoC_5H_{11}NO_{10}$: Mo, 28.1; C, 17.6; H, 3.3; N, 4.1; O_2^{2-}, 18.7. Found: Mo, 27.4; C, 17.8; H, 3.2; N, 4.1; O_2^{2-}, 16.2.

Reaction of Molydenum Peroxide with Aspartic Acid. Attempts to prepare the complex with aspartic acid did not succeed. The product obtained at pH ca. 4.8 was an oil, from which needle-thin crystalline aggregates precipitated after 2−3 days. They decomposed explosively upon mild heating, and their analysis indicated the presence of a mixture containing some Mo−peroxo−aspartic acid product and Mo peroxides. At higher pH, various Mo(VI) peroxides crystallized, much as in the other preparations.

Trials with Cysteine. Various modifications of the synthetic procedures ended with fine powders, rendering variable analyses. These solids did not contain cysteine, nor cystine, which formed in the vanadium hydrogen peroxide solutions, where crystalline K_4[O-{$VO(O_2)_2$}$_2$cystine]·$2H_2O$ was obtained.[10]

Physical Measurements and Analyses. Infrared spectra of Nujol and hexachlorobutadiene mulls were recorded with a Perkin-Elmer Model 983 spectrophotometer. Electronic absorption spectra were recorded on a Beckman Acta VI spectrophotometer. ^1H and ^{13}C NMR spectra, relative to an external $(CH_3)_4Si$ standard, were obtained on a Varian FT-80A 80 MHz spectrometer, at room temperature in tubes of diameter 10 mm. The data are results of several independent runs, with a precision of ±0.03 ppm or better.

C, H, N, K, V, and Mo analyses were performed by Atlantic Microlab, Inc., and Galbraith Laboratories, Inc. Molybdenum was determined by ignition to MoO_3. Peroxides were determined by Ce(IV) titration on a Brinkmann E536 potentiograph.

X-ray Structure Determination. Cell dimensions and space group data were obtained by standard methods; crystallographic data are given in Table 1. The intensities of three standard reflections showed no greater fluctuations during this data collection than those expected form Poisson statistics. The raw intensity data were corrected for the Lorentz-polarization effect and absorption. A three-dimensional Patterson synthesis was used to determine the heavy-atom position, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier synthesis. Full-matrix least-squares refinement was carried out as previously described.[11] Anisotropic temperature factors were introduced for the non-hydrogen atoms. A listing of the thermal parameters is available as Supporting Information. The principal programs used are as previously described.[11]

Results

Synthetic Chemistry and Solubility. Crystalline, yellow complexes of the $MoO(O_2)_2$(α-aa)(H_2O) series were all prepared from the acidic aqueous hydrogen peroxide solutions; however, the preparation procedures had to be modified for each α-amino acid. The glycine complex (**1**) is readily obtained in the pure state, does not decompose when heated in vacuo at 110 °C for hours, and is stable for months when standing over Drierite. The syntheses of the complexes **2**−**9** are less straightforward, and the complexes cannot be simply recrystallized. Repeated preparation and modification of the procedures regarding concentrations, temperature, and pH is the only way to obtain pure products. At higher pH a variety of Mo(VI) peroxides coprecipitate in the presence of potassium ions.[12] Complexes

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Table 1. Crystal Data for $MoO(O_2)_2(\alpha\text{-aa})(H_2O)$ for α-aa = Glycine (**1**), Alanine (**2**), and Proline (**3**)

	1	**2**	**3**
formula	$MoC_2H_7NO_8$	$MoC_3H_9NO_8$	$MoC_5H_{11}NO_8$
fw	269	283	309
space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a, Å	8.517(1)	10.727(3)	6.788(3)
b, Å	8.360(1)	8.026(2)	8.738(2)
c, Å	10.460(2)	10.794(4)	16.508(7)
β, deg	99.84(2)	110.81(2)	
V, Å^3	734	869	979
Z	4	4	4
d_{calcd}, g/cm^3	2.44	2.16	2.10
cryst size, mm	0.19 × 0.30 × 0.08	0.04 × 0.14 × 0.12	0.09 × 0.75 × 0.16
μ(Mo Kα), cm^{-1}	17.8	15.1	13.5
data collection instrument	Enraf-Nonius four-cycle CAD-4	Enraf-Nonius four-cycle CAD-4	Enraf-Nonius four-cycle CAD-4
radiation, monochromated in incident beam (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	23	23	23
scan method	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
data collection range (2θ), deg	$1.5 < 2\theta < 58$	$1.5 < 2\theta < 60$	$1.5 < 2\theta < 62$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2283, 1793	2677, 2270	2024, 1307
transm factors: max, min	0.783, 0.739	0.824, 0.765	0.748, 0.682
R^a	0.022	0.041	0.027
$R_w{}^b$	0.026	0.047	0.032
quality of fit indicator^c	1.0	1.3	1.1
largest shift/esd, final cycle	0.02 times its esd	0.14	0.16

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma^2$ ($|F_o|$). ^{c} Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table 2. Relevant Spectral Data for Complexes **1**−**9**

	infrared data (cm^{-1})						
complex	ν(OH)	δ(HOH)	ν(M═O)	ν(O−O)	ν_{asym}[M−O(O)$_2$]	ν_{sym}[M−O(O)$_2$]	UV−vis data (nm): λ_{max}
$MoO(O_2)_2$(glycine)(H_2O) (**1**)	3416	1666	969	878, 860	653	578	350
$MoO(O_2)_2$(alanine)(H_2O) (**2**)	3400	1655	978	880, 860	654	583	338
$MoO(O_2)_2$(proline)(H_2O) (**3**)	3422	1686	971	875, 862	656	583	340
$MoO(O_2)_2$(valine)(H_2O) (**4**)	3454	1667	976	870, 861	655	572	330
$MoO(O_2)_2$(leucine)(H_2O) (**5**)	3436	1692	970	870, 865	653	583	360
$MoO(O_2)_2$(serine)(H_2O) (**6**)	3400	1700 br	960	870, 855	650	580	370
$MoO(O_2)_2$(asparagine)(H_2O) (**7**)	3497	1688	962	884, 875	660	585	330
$MoO(O_2)_2$(glutamine)(H_2O) (**8**)	3430	1660	970	865 br	656	585	320
$MoO(O_2)_2$(glutamic acid)(H_2O) (**9**)	3410	1673	976	880, 867	660	585	325

2−**9** are less stable than **1**, and they decompose by losing peroxides and water on heating in vacuo.[13,14] In the solid state, however, they do not change for months if they are pure and are kept in a dry atmosphere. Decomposition of the compounds was followed by the peroxide analysis and recording of IR spectra. All of the complexes are moderately soluble in water and hydrogen peroxide, and slightly soluble in ethanol. They dissolve in DMSO with decomposition, some explosively. The aqueous solutions of all of the complexes are acidic. The pK_as of these solutions are of the order of the pK_as of the corresponding free α-amino acids. The pK_a values were determined potentiometrically.

Spectroscopy. The UV−visible spectra of the complexes in 0.1 M KCl aqueous solutions showed a broad absorption at 320, 315, and 315 nm for **7**, **8**, and **9**, respectively (ϵ ca. 1000). The resolution of the spectra of the complexes **1**−**6** in the aqueous solutions was very poor. The LMCT bands of the coordinated peroxo groups, expected in these spectra,[15] however, were obtained in the solid state, in the Nujol mulls. The results are given in Table 2.

IR spectra display characteristic differences between the spectra of the complexes and the spectra of the corresponding free α-amino acids. In addition, several strong bands, due to Mo═O, O−O, Mo−O(O_2), and coordinated water molecule vibrations, appear at approximately the same frequency in the spectra of all of the α-amino acid complexes. Comparison of these spectra was used to assign the selected vibrational frequencies, shown in Table 2. The region of OH and NH stretchings displays prominent bands. The free α-amino acids show no absorption down to about 3200 cm^{-1}; however, all of the molybdenum complexes display at ca. 3400 cm^{-1} sharp peaks, assigned to the OH stretchings of the coordinated water molecule. From 3332 to 3000 cm^{-1} follow the well-resolved NH stretching bands as expected from the zwitterionic RNH_3^+ group, and the amino group in the asparagine and glutamine. The asparagine spectrum of the molybdenum complex, for example, shows a well-resolved seven-peak absorption, replacing a single strong band at 3353 cm^{-1} and medium strong continuous broad absorption from 3200 to 3090 cm^{-1}, observed in the free asparagine. In the region between 1700 and 1400 cm^{-1} the characteristic shifts of the asymmetric and symmetric CO stretchings occur, due to the coordinated monodentate carboxylato group. The δ(HOH) is clearly resolved between 1690 and 1655 cm^{-1}. The crowding of deformation modes of HOH, CH, and NH vibrations prevents the assignment of a particular peak to the ν_{as}(COO). However, in the spectra of all of the complexes a general shift of the broad strong absorption to higher frequencies is observed in the region 1700−1600 cm^{-1},

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Table 3. ^{1}H and ^{13}C NMR Chemical Shifts and Assignment in D_2O[a]

$MoO(O_2)_2$(glycine)(H_2O)	$MoO(O_2)_2$(proline)(H_2O)	$MoO(O_2)_2$(valine)(H_2O)
	^{1}H	
3.67 CH_2	4.20 H(1) CH	3.78 H(1) CH
	3.30 H(4) CH_2	2.25 H(2) CH
	2.20 H(2) CH_2	1.03 H(2) CH_3
	2.00 H(3) CH_2	0.95 H(2) CH_3
	^{13}C	
171.10 CO	173.34 CO	172.85 CO
41.15 CH_2	60.90 C(1) CH	59.76 C(1) CH
	46.82 C(4) CH_2	29.41 C(2) CH
	28.85 C(2) CH_2	17.61 C(2) CH_3
	23.73 C(3) CH_2	17.08 C(2) CH_3

[a] δ(TMS) = 0.0 ppm. The protons are numbered according to the numbering scheme of the carbon atoms to which they are bound.

compared to the spectra of the corresponding α-amino acids. This shift is characteristic for the ν_{as}(CO) stretchings of the coordinated carboxylato groups.[17,18] ν_s(CO), on the other hand, occurring in a less crowded region of the spectra, can be easily detected as a single additional band at ca. 1400 cm^{-1}. In the free α-amino acids this band is found at ca. 1413 cm^{-1}. This shift to lower frequencies suggests that the monodentate zwitterion coordination, found by X-ray structure analysis in the glycine, alanine, and proline complexes, exists also in the other six α-amino acid complexes, **4**−**9**. Oxygens of the carboxylato group that are not coordinated to molybdenum are intermolecularly hydrogen bonded to either the amino group or the water molecule of the neighboring complex molecule. The COO stretching modes are therefore affected by coordination, as well as by intermolecular interactions. In general, however, the coordinated carboxylato group shows an increase in antisymmetric frequencies and a decrease in the frequency of symmetric vibrational modes.[17]

Very strong additional bands in the spectra of complexes originate in the O−O and Mo−O stretching vibrational modes,[6,15,18−21] listed in Table 2. Mo═O stretchings appear in the expected region at ca. 970 cm^{-1}. An intense doublet in the vicinity of 870 cm^{-1} represents the typical ν(O−O) of the coordinated peroxo groups. The M−O(O_2^{2-}) stretching modes are also clearly resolved as additional bands in the spectra of complexes. Most of the bands occurring in the spectra of free α-amino acids are slightly shifted and decreased in intensity in the spectra of the complexes. These changes reflect a changed environment for the coordinated zwitterion in the molybdenum complex. In the region of 400−200 cm^{-1} some weak additional bands appear in the spectra of all of the complexes, containing, among other modes, the vibrational modes associated with Mo−O stretchings.

The ^{1}H NMR chemical shifts of **1**, **3**, and **4** in D_2O solution are listed in Table 3. Spectra indicate that, within the NMR detection limits, the coordinated α-amino acid did not hydrolyze, and one complex species only is present in the solution. The peaks for all of the protons are well resolved. The spectra of the complexes resemble the spectra of the corresponding α-amino acids. Only small differences in chemical shifts are found, but distinct changes in the peak contours occur. Upon standing for a few hours, the D_2O solutions of the complexes become cloudy, and the ^{1}H spectra display several additional peaks, revealing the presence of the free α-amino acid, mixed with the complex species. The D_2O solutions were used only for ^{1}H NMR. For ^{13}C NMR spectra, D_2O solutions of all of the compounds were not stable and concentrated enough. To prevent precipitation during the experiment, a small amount of hydrogen peroxide had to be added to D_2O solutions. The ^{13}C chemical shifts of **1**, **3**, and **4** are given in Table 3. In agreement with the ^{1}H NMR evidence, ^{13}C spectra, too, indicate the presence of one complex species only. An upfield shift (ca. 0.6−2.6 ppm) is observed on comparison with the spectra of free α-amino acids, reflecting slight deshielding of carbons of the coordinated zwitterion. The largest upfield shift occurs, as expected, for the CO carbon, because the coordination of the carboxylato oxygen to molybdenum decreases the shielding of the CO carbon. The ^{95}Mo spectra could be obtained only in concentrated hydrogen peroxide (15%) solutions. Under these conditions peroxo molybdate species prevail, and a practically identical ^{95}Mo chemical shift was observed for complexes **1**−**6**.

Table 4. Positional Parameters and Their Estimated Standard Deviations for $MoO(O_2)_2$(glycine)(H_2O) (**1**)

atom	*x*	*y*	*z*
Mo	0.23037(3)	0.24010(3)	0.28833(2)
O	0.1190(3)	0.1467(3)	0.3834(2)
O(1p)	0.4092(3)	0.3177(3)	0.4142(2)
O(2p)	0.4422(3)	0.1583(3)	0.3628(2)
O(3p)	0.0722(3)	0.3535(3)	0.1653(2)
O(4p)	0.1407(3)	0.4529(3)	0.2761(2)
O(w)	0.3881(3)	0.3469(3)	0.1460(2)
O(1g)	0.2068(3)	0.0703(2)	0.1432(2)
O(2g)	0.2772(3)	−0.1513(3)	0.2611(2)
N(g)	0.2154(3)	−0.3457(3)	0.0502(3)
C(1g)	0.2293(3)	−0.0823(3)	0.1590(3)
C(2g)	0.1880(4)	−0.1717(4)	0.0315(3)
H(21g)	0.270(5)	−0.132(5)	−0.025(4)
H(22g)	0.080(5)	−0.145(5)	−0.006(4)
H(31g)	0.159(6)	−0.391(6)	0.102(4)
H(32g)	0.316(5)	−0.363(5)	0.077(4)
H(33g)	0.200(5)	−0.393(6)	−0.011(4)
H(1w)	0.485(5)	0.360(5)	0.174(4)
H(2w)	0.392(5)	0.293(6)	0.089(4)

X-ray Crystallography. A preliminary report on the structures of **1** and **3** was published some time ago.[9] Elaborate attempts over the years to obtain crystals suitable for an X-ray structure analysis of some other α-amino acid complexes ended with crystals of **2** only. We now report complete data for the structures of **1**−**3**.

Crystallographic parameters are summarized in Table 1, and the final positional parameters are given in Tables 4−6. The most important bond lengths and the nearest intermolecular contacts with the bond angles are listed in Tables 7−9. Figure 1 shows the structure and the labeling scheme of the alanine, and Figure 2 of the proline complex (the glycine is shown in the preliminary note[9]). All three of the structures consist of monomeric, distorted pentagonal bipyramidal molecules. The α-amino acid is coordinated in the form of a zwitterion, via one oxygen of the carboxylato group. In each complex the coordinated amino acid oxygen is coplanar with the four peroxo oxygens. This combined five-atom plane forms the base of a distorted pentagonal bipyramid, which has the "oxo" oxygen and the coordinated water molecule as apices. The molybdenum atom is displaced for about 0.36 Å out of this plane, toward the "oxo" oxygen. The pentagonal units are linked together

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Table 5. Positional Parameters and Their Estimated Standard Deviations for $MoO(O_2)_2$(alanine)(H_2O) (**2**)

atom	*x*	*y*	*z*
Mo	0.26581(4)	0.22275(5)	0.34829(4)
O	0.1517(4)	0.1370(6)	0.2158(4)
O(1p)	0.4056(4)	0.2834(5)	0.2806(3)
O(2p)	0.4276(3)	0.1144(5)	0.3419(3)
O(3p)	0.2134(4)	0.4511(5)	0.3363(4)
O(4p)	0.1645(4)	0.3593(5)	0.4266(4)
O(w)	0.4321(3)	0.3149(5)	0.5485(3)
O(1)	0.2521(3)	0.0513(4)	0.4843(3)
O(2)	0.3150(4)	−0.1779(5)	0.4025(3)
N	0.3142(5)	−0.3681(5)	0.6086(4)
C(1)	0.2784(4)	−0.1057(6)	0.4838(4)
C(2)	0.2551(5)	−0.1989(6)	0.5969(5)
C(3)	0.1093(6)	−0.2128(9)	0.5780(7)
H(1n)	0.293(7)	−0.408(9)	0.548(7)
H(2n)	0.415(9)	−0.334(13)	0.620(9)
H(3n)	0.304(7)	−0.398(10)	0.678(7)
H(1w)	0.411(5)	0.230(7)	0.112(5)
H(2w)	0.497(6)	0.235(8)	0.054(5)
H(2c)	0.299(5)	−0.157(7)	0.680(5)
H(1m)	0.062(6)	−0.266(8)	0.486(6)
H(2m)	0.089(7)	−0.116(10)	0.588(7)
H(3m)	0.095(6)	−0.255(9)	0.673(6)

Table 6. Positional Parameters and Their Estimated Standard Deviations for $MoO(O_2)_2$(proline)(H_2O) (**3**)

atom	*x*	*y*	*z*
Mo	0.05682(7)	0.09657(6)	0.12320(3)
O	0.0810(7)	−0.0613(5)	0.1796(2)
O(1p)	0.1230(8)	0.2572(6)	0.1980(3)
O(2p)	0.2940(7)	0.2090(6)	0.1487(3)
O(3p)	−0.1878(7)	0.0466(5)	0.0642(3)
O(4p)	−0.2201(7)	0.1384(5)	0.1372(3)
O(w)	0.0336(8)	0.3048(5)	0.0334(3)
O(1)	0.2128(6)	0.0204(5)	0.0242(2)
O(2)	0.0896(8)	−0.2188(5)	0.0137(2)
N	0.2126(8)	−0.2582(5)	−0.1386(3)
C(1)	0.1764(8)	−0.1076(7)	−0.0136(3)
C(2)	0.2456(8)	−0.1020(7)	−0.1013(3)
C(4)	0.0032(11)	−0.2628(9)	−0.1694(4)
C(5)	−0.0720(11)	−0.0978(11)	−0.1634(4)
C(6)	0.1103(11)	−0.0014(7)	−0.1515(4)
H(2)	0.400(8)	−0.072(6)	−0.109(3)
H(31)	0.231(10)	−0.318(7)	−0.107(4)
H(32)	0.279(10)	−0.255(7)	−0.184(4)
H(41)	−0.066(14)	−0.336(9)	−0.140(5)
H(42)	−0.008(12)	−0.298(8)	−0.226(4)
H(51)	−0.166(12)	−0.072(10)	−0.203(5)
H(52)	−0.169(12)	−0.110(10)	−0.109(5)
H(61)	0.081(10)	0.095(8)	−0.123(4)
H(62)	0.0170(13)	0.006(10)	−0.202(5)
H(w1)	−0.078(19)	0.352(13)	0.004(7)
H(w2)	0.126(14)	0.343(10)	0.009(5)

by intermolecular hydrogen bonding to form an infinite polymer network. These structures represent the typical stereochemistry of Mo(VI) peroxo complexes.[2,3,6−9,12,18−33]

Table 7. Selected Interatomic Distances (Å) and Bond Angles (deg) for $MoO(O_2)_2$(glycine)(H_2O) (**1**)

Interatomic Distances (Å)			
Mo−O	1.680(1)	N(g)−C(2g)	1.480(1)
Mo−O(1p)	1.947(1)	O(1p)−H(2w)	2.07(1)(a)[a]
Mo−O(2p)	1.962(1)	O(2p)−H(32g)	2.06(1)(b)[a]
Mo−O(3p)	1.943(1)	O(w)−H(1w)	0.83(1)
Mo−O(4p)	1.932(1)	O(w)−H(2w)	0.76(1)
Mo−O(w)	2.346(1)	O(2g)−H(1w)	2.03(1)(c)[a]
Mo−O(1g)	2.063(1)	N(g)−H(31g)	0.87(1)
O(1p)−O(2p)	1.481(1)	N(g)−H(32g)	0.87(1)
O(3p)−O(4p)	1.464(1)	N(g)−H(33g)	0.74(1)
O(1g)−C(1g)	1.296(1)	C(2g)−H(21g)	1.05(1)
O(2g)−C(1g)	1.221(1)	C(2g)−H(22g)	0.96(1)
C(1g)−C(2g)	1.517(g)		
Bond Angles (deg)			
O−Mo−O(1p)	102.16(3)	O(3p)−Mo−O(4p)	44.39(3)
O−Mo−O(2p)	100.19(3)	O(3p)−Mo−O(w)	78.54(3)
O−Mo−O(3p)	102.78(3)	O(3p)−Mo−O(1g)	83.03(3)
O−Mo−O(4p)	102.15(3)	O(4p)−Mo−O(w)	82.54(3)
O−Mo−O(w)	174.53(3)	O(4p)−Mo−O(1g)	126.66(3)
O−Mo−O(1g)	97.01(3)	O(w)−Mo−O(1g)	77.83(2)
O(1p)−Mo−O(2p)	44.54(3)	Mo−O(1p)−O(2p)	68.28(3)
O(1p)−Mo−O(3p)	131.23(3)	Mo−O(2p)−O(1p)	67.18(4)
O(1p)−Mo−O(4p)	89.59(3)	Mo−O(3p)−O(4p)	67.39(3)
O(1p)−Mo−O(w)	80.52(2)	Mo−O(4p)−O(3p)	68.22(3)
O(1p)−Mo−O(1g)	133.91(3)	Mo−O(1g)−C(1g)	126.12(5)
O(2p)−Mo−O(3p)	156.82(3)	O(1g)−C(1g)−O(2g)	126.61(8)
O(2p)−Mo−O(4p)	132.35(3)	O(1g)−C(1g)−C(2g)	111.48(7)
O(2p)−Mo−O(w)	78.30(3)	O(2g)−C(1g)−C(2g)	121.91(7)
O(2p)−Mo−O(1g)	91.15(3)	C(1g)−C(2g)−N(g)	111.15(7)

[a] Intermolecular hydrogen bonds; symmetry transformations: (a) *x*, $^1/_2 - y$, $^1/_2 + z$; (b) $1 - x$, $^1/_2 + y$, $^1/_2 - z$; (c) $1 - x$, $y - ^1/_2$, $^1/_2 - z$.

Table 8. Selected Interatomic Distances (Å) and Bond Angles (deg) for $MoO(O_2)_2$(alanine)(H_2O) (**2**)

Interatomic Distances (Å)			
Mo−O	1.665(2)	O(1p)−O(2p)	1.491(3)
Mo−O(1p)	1.948(2)	O(3p)−O(4p)	1.459(3)
Mo−O(2p)	1.964(2)	O(1)−C(1)	1.291(3)
Mo−O(3p)	1.908(2)	O(2)−C(1)	1.226(3)
Mo−O(4p)	1.936(2)	N−C(2)	1.485(3)
Mo−O(w)	2.379(2)	C(1)−C(2)	1.526(4)
Mo−O(1)	2.055(2)	C(2)−C(3)	1.507(4)
Bond Angles (deg)			
O−Mo−O(1p)	102.12(10)	O(3p)−Mo−O(w)	82.56(8)
O−Mo−O(2p)	100.13(10)	O(3p)−Mo−O(1)	126.69(9)
O−Mo−O(3p)	103.30(11)	O(4p)−Mo−O(w)	77.48(8)
O−Mo−O(4p)	104.70(10)	O(4p)−Mo−O(1)	82.74(8)
O−Mo−O(w)	173.55(10)	O(w)−Mo−O(1)	77.29(8)
O−Mo−O(1)	96.87(10)	Mo−O(1p)−O(2p)	68.18(11)
O(1p)−Mo−O(2p)	44.79(9)	Mo−O(2p)−O(1p)	67.04(11)
O(1p)−Mo−O(3p)	88.96(10)	Mo−O(3p)−O(4p)	68.71(11)
O(1p)−Mo−O(4p)	130.39(9)	Mo−O(4p)−O(3p)	66.67(12)
O(1p)−Mo−O(w)	80.48(8)	Mo−O(1)−C(1)	125.4(2)
O(1p)−Mo−O(1)	134.02(9)	O(1)−C(1)−O(2)	126.2(2)
O(2p)−Mo−O(3p)	131.72(10)	O(1)−C(1)−C(2)	112.1(2)
O(2p)−Mo−O(4p)	154.93(9)	O(2)−C(1)−C(2)	121.7(2)
O(2p)−Mo−O(w)	77.46(8)	N−C(2)−C(1)	109.2(2)
O(2p)−Mo−O(1)	90.97(8)	N−C(2)−C(3)	109.5(2)
O(3p)−Mo−O(4p)	44.62(9)	C(1)−C(2)−C(3)	112.6(2)

Characteristic bond lengths of structures **1**−**3** are collected in Table 10. Data for some previously reported peroxo complexes are included for later discussion. As shown in Table 10, the O−O bond lengths differ slightly in the two peroxo groups of a diperoxo complex. They fall in the expected range for all of the oxodiperoxo Mo(VI) complexes: monomeric,[18,23−25] bridged dimers[21,26,27,32] or trimers,[6] and even the diperoxohep-

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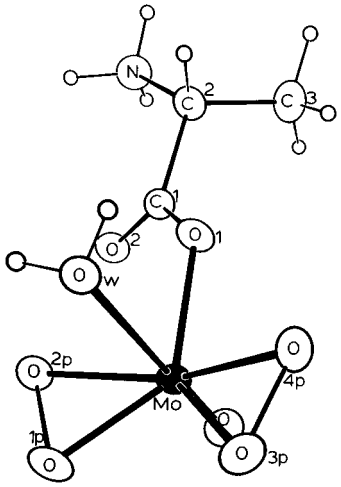

Figure 1. Structure and labeling scheme for $MoO(O_2)_2$(Alanine)(H_2O) (**2**).

Table 9. Selected Interatomic Distances (Å) and Bond Angles (deg) for $MoO(O_2)_2$(proline)(H_2O) (**3**)

Interatomic Distances (Å)			
Mo−O	1.673(2)	O(1)−C(1)	1.305(4)
Mo−O(1p)	1.923(2)	O(2)−C(1)	1.222(4)
Mo−O(2p)	1.932(2)	C(1)−C(2)	1.522(4)
Mo−O(3p)	1.974(2)	C(2)−N	1.514(4)
Mo−O(4p)	1.929(2)	C(2)−C(6)	1.518(4)
Mo−O(w)	2.353(2)	N−C(4)	1.510(5)
Mo−O(1)	2.058(2)	C(4)−C(5)	1.534(6)
O(1p)−O(2p)	1.479(3)	C(5)−C(6)	1.510(6)
O(3p)−O(4p)	1.464(3)		
Bond Angles (deg)			
O−Mo−O(1p)	102.79(10)	O(4p)−Mo−O(1)	131.13(9)
O−Mo−O(2p)	102.47(11)	O(w)−Mo−O(1)	77.51(9)
O−Mo−O(3p)	100.08(10)	Mo−O(1p)−O(2p)	67.78(12)
O−Mo−O(4p)	100.65(11)	Mo−O(2p)−O(1p)	67.11(13)
O−Mo−O(w)	174.57(10)	Mo−O(3p)−O(4p)	66.34(12)
O−Mo−O(1)	97.21(10)	Mo−O(4p)−O(3p)	69.61(12)
O(1p)−Mo−O(2p)	45.11(10)	Mo−O(1)−O(2)	99.77(10)
O(1p)−Mo−O(3p)	132.43(10)	Mo−O(1)−C(1)	124.0(2)
O(1p)−Mo−O(4p)	90.70(10)	O(1)−C(1)−O(2)	126.6(2)
O(1p)−Mo−O(w)	81.70(10)	O(1)−C(1)−C(2)	111.6(3)
O(1p)−Mo−O(1)	128.76(10)	O(2)−C(1)−C(2)	121.7(3)
O(2p)−Mo−O(3p)	157.06(10)	C(1)−C(2)−N	108.2(3)
O(2p)−Mo−O(4p)	133.59(11)	C(1)−C(2)−C(6)	110.5(3)
O(2p)−Mo−O(w)	78.47(10)	N−C(2)−C(6)	102.1(2)
O(2p)−Mo−O(1)	84.78(9)	C(2)−N−C(4)	107.5(3)
O(3p)−Mo−O(4p)	44.05(9)	N−C(4)−C(5)	105.5(3)
O(3p)−Mo−O(w)	78.69(10)	C(4)−C(5)−C(6)	105.1(3)
O(3p)−Mo−O(1)	88.24(9)	C(2)−C(6)−C(5)	104.1(3)
O(4p)−Mo−O(w)	82.19(10)		

tamolybdates.[12] In the oxomonoperoxo Mo(VI) complexes, with or without a heteroligand, the O−O bond is shorter.[8,30,31] The Mo−O(O_2^{2-}) bond lengths also fall into the expected range: between 1.908(2) and 1.974(2) Å. The two Mo−O(O_2^{2-}) bonds in a coordinated peroxo group are not equal. The longer bond is located next to the carboxylato oxygen, and the shorter next to the neighboring peroxo oxygen. Mo=O bonds are remarkably similar in all of the mono- and diperoxo complexes.[34] The Mo−O(H_2O) bond is longer than in the diperoxomolybdates(VI) with no heteroligand,[26,32] similar to the distance found in $MoO(O_2)_2$(HMPT)(H_2O).[25] The O=Mo−OH_2 axis is less distorted from linearity than in the other complexes, with the angle (ca. 174°) slightly tilted away from the equatorial carboxylato oxygen. The two carbon−oxygen bonds in the monodentately coordinated carboxylato group differ in bond length more than in the [ON] bidentate complexes [Ni(gly)$_2$-

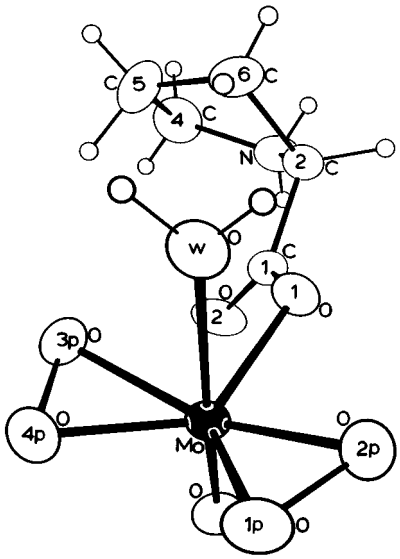

Figure 2. Structure and labeling scheme for $MoO(O_2)_2$(proline)(H_2O) (**3**).

$(H_2O)_2$][36] and [Cu(ala)$_2H_2O$], where the (C=O bond length is 1.234(4) Å, and C−O (coordinated) 1.291(3) Å).[37]

Discussion

The α-amino acid metal complexes have been investigated since the Werner days,[38,39] mainly for M(II) = Co, Ni, Cu, Zn, Pt. Crystalline Mo(VI) complexes with α-amino acids included in this study have not been reported. The $MoO(O_2)_2$(α-aa)-(H_2O) complexes described here represent in addition the first peroxo−α-amino acid ligand combination in a complex. They demonstrate that α-amino acids present in **1**−**9** remain unchanged in the acid hydrogen peroxide solutions, where the malato and malonato ions, for example, convert catalytically to oxalates.[7] Under these conditions Mo(VI) incorporated the zwitterion via an oxygen, which is not surprising because of the Mo(VI) preference and affinity for oxygen. The monodentate carboxylato group coordination was found in a few α-amino acid complexes prepared at low pH, although bidentate chelation via an oxygen and the nitrogen is more common.[35,36]

The three structures $MoO(O_2)_2$(α-aa)(H_2O), α-aa = gly (**1**), ala (**2**), and pro (**3**), represent the classical stereochemistry of Mo(VI) peroxo complexes: a distorted pentagonal bipyramid.[2,3,6−9,12,18−33] Relevant bond lengths (listed in Table 10) demonstrate characteristic structural features for selected oxodiperoxo Mo(VI) structures (with reasonable estimated standard deviations). In addition to the structures **1**−**3**, the following diperoxo complexes, reported previously, are listed for comparison: $K_2MoO(O_2)_2C_2O_4$,[7] $MoO(O_2)_2$(HMPT)(H_2O),[25] $MoO(O_2)_2$[O(P)N],[33] $H[MoO(O_2)_2(C_5H_4NCO_2)]\cdot 2C_5H_4NCO_2H\bullet H_2O$,[18] and $(C_3H_5N_2)_2[O\{MoO(O_2)_2H_2O\}_2]$.[26] Table 10 clearly illustrates the nonsymmetrical Mo−O(O_2^{2-}) bonds in the coordinated peroxo groups, with the bond length difference ca. 0.006(2)−0.045(2) Å. This difference was mentioned before,[6,24] and the electronic causes for the distortion in $M(O_2)_4^{n-}$ were

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Table 10. Pertinent Bond Lengths in Selected Mo(Vl) Diperoxo Compounds (Å)

complex	(O−O)/Mo−O(O_2^{2-})		Mo═O	Mo−OH_2	Mo−O(R)	C−O(Mo)	C═O	ref
$MoO(O_2)_2$(glycine) H_2O	1.464(1)	1.481(1)						
	1.943(1)	1.962(1)	1.680(1)	2.346(1)	2.063(1)	1.296(1)	1.221(1)	
	1.932(1)	1.947(1)						
$MoO(O_2)_2$(alanine) H_2O	1.491(3)	1.459(3)						
	1.964(2)	1.936(2)	1.665(2)	2.379(2)	2.055(2)	1.291(3)	1.226(3)	
	1.948(1)	1.908(2)						
$MoO(O_2)_2$(proline) H_2O	1.464(3)	1.479(3)						
	1.974(2)	1.932(2)	1.673(2)	2.353(2)	2.058(2)	1.305(4)	1.222(4)	
	1.924(2)	1.923(2)						
$K_2[MoO(O_2)_2C_2O_4]$	1.466(2)	1.480(2)						
	1.961(1)	1.958(1)	1.676(1)		2.051(1)	1.301(3)	1.210(2)	7
	1.941(1)	1.941(1)						
$MoO(O_2)_2$(HMPT)(H_2O)	1.498(8)	1.494(8)						
	1.952(5)	1.929(5)	1.662	2.347(5)				25
	1.935(5)	1.952(5)						
$H[MoO(O_2)_2(C_5H_4NCO_2)]$	1.462(3)	1.467(3)						
	1.923(2)	1.954(2)	1.685(2)					18
	1.948(2)	1.914(2)						
$MoO(O_2)_2$[O(P)N]	1.475(3)	1.480(3)						
	1.907(2)	1.940(2)	1.682(2)					33
	1.948(2)	1.904(2)						
$(C_3H_5N_2)_2[O\{MoO(O_2)_2H_2O\}_2]$	1.466(4)	1.466(4)						
	1.962(2)	1.940(2)	1.682(2)	2.441(2)				26
	1.952(1)	1.952(2)						

Table 11. Correlations between Bond Length and Spectral Data in $MoO(O_2)_2$(α-aa)(H_2O) Complexes

complex	Mo═O (Å)	ν(Mo═O) (cm^{-1})	(O−O) (Å)	ν(O−O) (cm^{-1})	mean Mo−O(O_2^{2-}) (Å)	λ_{max} (nm)
$MoO(O_2)_2$(glycine)(H_2O)	1.680	969	1.464	878	1.946	350
			1.481	860		
$MoO(O_2)_2$(alanine)(H_2O)	1.665	978	1.459	880	1.939	338
			1.491	860		
$MoO(O_2)_2$(proline)(H_2O)	1.673	971	1.464	875	1.939	340
			1.479	862		

calculated.[40] The longer bond is located regularly next to the fifth donor atom in the pentagonal plane, and the shorter by the other peroxo group. The bonds differ less in the peroxo complexes with no heteroligands.[26,32] Intra- and intermolecular hydrogen bonding and steric effects are obviously part of the reason for this bond length variation. The O−O bond length difference does not seem to be related to the nonsymmetry of Mo−O(O_2^{2-}) bonds. The magnitude of the bond variation does not appear to depend upon the deviation from linearity of the O═Mo−OH_2 angle, either. In general, the chelating heteroligands generate a larger deformation of the pentagonal bipyramid and contribute to the tilting of the O═Mo−OH_2 angle away from the fifth donor in the plane, toward the peroxo side. All of these structural features must be related (among other factors) to the specific oxygen transfer ability[8] and the catalytic selectivity[5] observed for several peroxo Mo(VI) complexes.[4,5]

The synthesis, crystallization, and behavior of $MoO(O_2)_2$(α-aa)(H_2O) complexes in solution were complicated by the highly pH and concentration sensitive coprecipitation of various Mo(VI) peroxo species. The coordinated zwitterion lacks the ability, provided by some chelating heteroligands, to stabilize the peroxo ligand sphere. The stable, easily crystallized glycine derivative **1** is an exception, possibly for steric reasons, which also apply to some extent in the cases of **2** and **3**. IR spectra remained an important source of information on the nature of **4**−**9**, since the X-ray structure analysis was not available. On the basis of the structures of **1**−**3** only, however, a correlation between particular bond lengths and the corresponding stretching frequencies in the IR spectra, as well as the LMCT bands in UV−visible spectra, has been observed. The data are shown in Table 11. The shorter the bond, the higher the vibrational energy for Mo═O and O−O bonds, as expected. The longer the mean Mo−O(O_2^{2-}) bond, the lower the energy of the LMCT bands. These simple and logical correlations can be perturbed by a number of factors which affect the bond length (e.g., hydrogen bonding and sterical effect) and/or vibrational frequency (e.g., coupling with α-amino acid modes). Nevertheless, these three isostructural complexes serve as a start in the search for analogous structure/spectra correlations to be obtained from a larger number of comparable complexes synthesized in the future, with more accurate spectral data. Observations of this kind may well serve the purpose of relating the reactivity and catalytic properties of peroxo complexes to their measurable physical properties.

Our interest in the peroxo heteroligand Mo(VI) complexes has been closely related to our investigations of vanadium(V)[41] and earlier Nb(V) and Ta(V) heteroligand peroxo complexes.[42] A comparison of the peroxo complexes of these metal ions brings to mind the intriguing diagonal relationship among the transition metals. The structure and properties of the V(V) peroxo complexes are much more similar to those of analogous Mo(VI) complexes than to those of analogous Nb(V) complexes. The pentagonal bipyramid is the common stereochemistry for both V(V) and Mo(VI), whereas Nb(V) displays 8-coordinated dodecahedral polyhedra. Examples are peroxo complexes with polycarboxylates, aminopolycarboxylates, bipyridyl, and *o*-phenanthroline. A terminal oxo group is invariably present in V(V) and Mo(VI) complexes, and it does not occur in peroxo heteroligand niobates(V). Finally, the oxygen transfer ability

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and the catalytic capacity, observed for V(V) and Mo(VI) peroxo complexes,[4−6] have no parallel in Nb(V) peroxo chemistry.

Along with this "diagonal similarity" there are distinct differences between V(V) and Mo(VI) peroxo chemistry. Apart from the difference in the oxygen transfer and the specific catalytic ability, the two metal ions vary with regard to the reactivity involving assorted heteroligands. For example, consider reactions of metal peroxo systems with α-amino acids. Mo(VI) forms, under controlled conditions, pure $MoO(O_2)_2$(α-aa)(H_2O) complexes **1**−**9**, but attempts to prepare analogous V(V) complexes invariably ended with the precipitation of yellow peroxo vanadates(V) without the α-amino acid. In addition, reduction to V(IV) (blue solutions) occurred upon standing of aqueous V(V) reaction mixtures. The story involving cysteine is different. After a vigorous reaction, crystalline cystine complexes, $M(I)_4[O\{VO(O_2)_2\}_2$cystine$]\cdot 2H_2O$, were obtained from the V(V) peroxo solutions.[10] Under analogous conditions, from the Mo(VI) hydrogen peroxide solutions with cysteine were obtained fine powdery precipitates. Repeated preparations did not yield powders with reproducible analyses. These powders did not contain cysteine nor cystine, but a mixture of products from obviously very complex reactions.

Molybdenum biological functions are involved in more than 30 distinct enzymes,[2,43] none of which has so far been related in any way to the Mo(VI) peroxide chemistry. On the other hand, the interaction of α-amino acids with molybdenum under various conditions is indeed of interest in biological chemistry. Recently, the crystal structure of the molybdoenzyme DMSO reductase was reported.[44] The structure revealed that the side chain oxygen of Ser^{147} is coordinated to molybdenum in the oxidized and reduced state of this enzyme. This observation certainly presents an incentive to obtain crystals and an X-ray structure of $MoO(O_2)_2$(serine)(H_2O), as well as to synthesize some molybdenum complexes containing coordinated serine. Mo(VI) interaction with α-amino acids, with or without peroxides, will remain an interesting topic to study for some time to come.

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Supporting Information Available: Listing of thermal parameters for **1**−**3** (6 pages). Ordering information is given on any current masthead page.

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