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Synthesis and Characterization of Osmyl–Amino Acid Complexes. Molecular Structure of *trans*-Dioxobis(glycinato)osmium(VI), $OsO_2(NH_2CH_2COO)_2$

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Received July 22, 1980

The synthesis and characterization of stable and well-defined osmium(VI)–amino acid complexes is reported for the first time. The reaction of OsO_4 with glycine, DL-alanine, DL-valine, DL-leucine, DL-isoleucine, and DL-phenylalanine leads to the formation of dioxobis(amino acidato)osmium(VI) complexes, which are isolable intermediates in a complex reaction sequence. The structure of the glycinato compound has been determined by X-ray diffraction. Crystals of the complex belong to the monoclinic space group $P2_1c$ with a = 5.041 (1) Å, b = 7.210 (2) Å, c = 10.885 (2) Å, β = 101.68 (1)°, V = 387.4 Å^3, and Z = 2. Mo Kα radiation of λ = 0.710 73 Å was used and the structure solved by determining the position of the osmium atoms with use of the Patterson heavy-atom method and then locating other atoms in succeeding difference Fourier syntheses to R = 0.028 for 1441 reflections. The molecule is composed of two deprotonated $NH_2CH_2COO^-$ ions chelated to a linear O–Os–O moiety through oxygen and nitrogen atoms. The Os–O distance of 1.731 (3) Å indicates the presence of an osmyl group. The two nitrogen atoms are trans to each other, and the molecule has a center of symmetry. Elemental analyses indicate that all six amino acids produce similar complexes. Infrared spectra of the complexes from 300 to 4000 cm^{-1} exhibit features common to those reported for planar amino acidato complexes of other transition metals. Although ambiguity in assignments of some important vibrational modes cannot be resolved, the spectral data indicate that all six reported complexes have similar structures.

Introduction

The extensive use of osmium tetroxide as a powerful tissue fixative and staining reagent has stimulated studies of its reactivity toward components of living organisms.[1] While satisfactory understanding of the interaction of OsO_4 with lipids[1,2] and nucleic acids[3] has been reached, very little is known concerning its reactivity with amino acids and proteins.[4-11] The reactions with amino acids include deamination, oxidation of side-chain functional groups, and fragmentation of a chain or ring.[5] The final product is a mixture of species, only some of which have been identified so far. It has been found that oxidation at the α-carbon proceeds according to[5]

$$RCH(NH_2)COOH \rightarrow RC(=O)COOH \rightarrow RCOOH$$

Osmium is reduced in these reactions to lower oxidation states with the eventual product being dark, opaque solutions containing a mixture of components. The nature of the resulting osmium compounds is obscure, and they have been referred to as simple or polymeric complexes,[6,7] hydrated osmium dioxide,[8,10] and intractable solids.[12] No successful separation of characterizable osmium compounds from the reaction mixture has ever been accomplished. Some other studies associated with osmium–amino acid systems have involved the formation of complexes with Os(IV),[13] the synthesis of complexes with blocked α-amino groups,[12] kinetic studies of OsO_4 reactions with tryptophan deriviatives,[14] and the oxidation of amino acids by ferricyanide with OsO_4 as a catalyst.[15]

This report describes the synthesis and characterization of dioxobis(amino acidato)osmium(VI) complexes. They are prepared by direct combination of OsO_4 and the amino acid in water. They are the first verifiable complexes separated from such systems. Results of an X-ray crystallographic study of one of the complexes are described, and important infrared spectral assignments are discussed for several examples.

Results and Discussion

The reaction between osmium tetroxide and amino acids with hydrocarbon R groups in water at room temperature is a slow process accompanied by changes in the appearance of the solution. The first stage is the formation of brightly colored crystalline precipitates. Six amino acids, i.e., glycine, alanine, valine, leucine, isoleucine, and phenylalanine (all except the first were DL forms), were investigated. The rate of formation of the precipitate decreases with an increase in their molecular weight. Thus the first two give 50–100 mg of the product overnight while for the remaining four it takes several days to produce comparable amounts of the compound.

At elevated temperatures (around 50 °C, above that point the liquid turns dark rapidly) about 80–100 mg of the product is obtained within several hours. Elemental analyses of the precipitates are given in Table I. They indicate that the compounds are of the same general type: two molecules of deprotonated acid attached to an OsO_2 unit (abbreviations: glycinato, gly; alaninato, ala; valinato, val; leucinato, leu; isoleucinato, ile; phenylalaninato, phe; amino acidato, aa). Glycinato and alaninato complexes crystallize in the form of well-developed needles while the others yield fine powders. The use of racemic DL forms may result in mixed crystals and be responsible for the lack of crystallinity.

Solubility and Reactivity of the Complexes. The compounds are hydrophobic. They adhere to glass in the presence of water and cannot be rinsed off easily. The opposite is observed with

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0020-1669/81/1320-2023$01.25/0

Table I. Elemental Analyses of $OsO_2(aa)_2$ Complexes

ligand	mol wt	%C exptl	%C calcd	%H exptl	%H calcd	%N exptl	%N calcd	%Os exptl	%Os calcd	color
glycine	370	13.21	12.97	2.26	2.16	7.71	7.57	50.2	51.35	red
alanine	398	18.04	18.09	3.24	3.02	7.03	7.04	46.4	47.74	light brown
valine	454	26.49	26.43	4.53	4.40	6.18	6.17	40.6	41.85	yellow
leucine	482	29.83	29.88	5.17	4.98	5.83	5.81	38.8	39.41	yellow
isoleucine	482	30.05	29.88	5.07	4.98	5.86	5.81	39.6	39.41	yellow
phenylalanine	550	39.65	39.27	3.79	3.64	5.02	5.09	34.6	34.55	yellow-grey

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $OsO_2(gly)_2$[a,b]

	x	y	z	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Os	0.0000	0.0000	0.0000	0.01037 (4)	0.00554 (2)	0.00233 (1)	0.0008 (1)	0.00304 (3)	0.00071 (5)
O(1)	0.2932 (5)	0.1310 (4)	0.0173 (3)	0.0129 (8)	0.0082 (4)	0.0044 (2)	−0.002 (1)	0.0032 (6)	0.0017 (5)
O(2)	0.0135 (6)	−0.0469 (4)	−0.1833 (3)	0.0178 (9)	0.0102 (4)	0.0030 (2)	0.011 (1)	0.0043 (6)	0.0012 (5)
O(3)	−0.1979 (9)	0.0083 (4)	−0.3790 (3)	0.0387 (15)	0.0110 (6)	0.0029 (2)	0.011 (2)	0.0027 (8)	0.0003 (7)
N(1)	−0.2291 (6)	0.2263 (4)	−0.0880 (3)	0.0154 (9)	0.0059 (4)	0.0030 (2)	0.002 (1)	0.0037 (6)	0.0003 (5)
C(1)	−0.1745 (9)	0.0367 (5)	−0.2668 (4)	0.018 (1)	0.0060 (6)	0.0030 (2)	0.000 (1)	0.0026 (8)	0.0004 (5)
C(2)	−0.3604 (7)	0.1661 (5)	−0.2160 (3)	0.013 (1)	0.0062 (5)	0.0030 (2)	0.000 (1)	0.0010 (7)	0.0010 (6)

	x	y	z	B, Å²		x	y	z	B, Å²
H(1)	−0.099 (9)	0.319 (6)	−0.088 (4)	1.6 (10)	H(3)	−0.393 (10)	0.265 (6)	−0.271 (4)	1.7 (10)
H(2)	−0.322 (9)	0.271 (6)	−0.055 (4)	0.6 (8)	H(4)	−0.515 (10)	0.105 (8)	−0.206 (4)	2.7 (12)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta(1,1)*h^2 + \beta(2,2)*k^2 + \beta(3,3)*l^2 + \beta(1,2)*hk + \beta(1,3)*hl + \beta(2,3)*kl)]$. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Bond Distances (Å) for $OsO_2(gly)_2$[a]

Os-O(1)	1.731 (3)	N(1)-H(1)	0.93 (5)
Os-O(2)	2.038 (3)	N(1)-H(2)	0.72 (4)
Os-N(1)	2.114 (3)	C(1)-C(2)	1.505 (5)
O(2)-C(1)	1.319 (5)	C(2)-H(3)	0.93 (5)
O(3)-C(1)	1.220 (5)	C(2)-H(4)	0.92 (5)
N(1)-C(2)	1.481 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Angles (Deg) for $OsO_2(gly)_2$[a,b]

O(1)-Os-O(1)′	180.0	Os-N(1)-H(1)	103 (3)
O(1)-Os-O(2)	90.0 (1)	Os-N(1)-H(2)	118 (3)
O(1)-Os-N(1)	90.3 (1)	H(1)-N(1)-H(2)	102 (4)
O(2)-Os-O(2)′	180.0	O(2)-C(1)-O(3)	121.6 (4)
O(2)-Os-N(1)	78.9 (1)	O(2)-C(1)-C(2)	116.4 (3)
N(1)-Os-N(1)′	180.0	C(1)-C(2)-H(3)	106 (3)
Os-O(2)-C(1)	115.9 (2)	C(1)-C(2)-H(4)	111 (4)
Os-N(1)-C(2)	107.4 (2)	H(3)-C(2)-H(4)	114 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Primed and unprimed atoms are related by the inversion.

Table V. Intermolecular Contacts (Å) Up to 2.50 Å in the Crystal Lattice of $OsO_2(gly)_2$[a]

O(1)-H(2)	2.454
O(2)-H(3)	2.477
O(3)-H(1)	2.112
O(3)-H(2)	2.475

[a] Estimated standard deviations were not calculated.

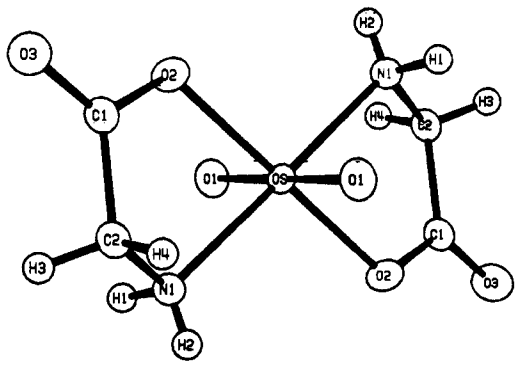

Figure 1. Stereoview of the $OsO_2(gly)_2$ molecule. Thermal ellipsoids enclose 50% of the probability distribution. The hydrogen atoms have been assigned arbitrary thermal parameters for clarity.

organic solvents. The dry materials are stable and may be stored for weeks without special precautions. However, crystals of $OsO_2(gly)_2$ develop black inclusions upon prolonged storage, indicating disproportionation.

The complexes are not reversibly soluble in any common solvent. They react with polar liquids, and a conversion into a variety of soluble, colored species takes place. The rate of the solid disappearance is very slow, even at elevated temperatures, with solvents like acetone and alcohol, while pyridine, Me_2SO, and concentrated H_2SO_4 cause almost instantenuous solubilization. The compounds are intermediates in a reaction sequence that involves several consecutive and competitive stages. When they are not separated from a reacting OsO_4–amino acid mixture, the liquid phase eventually becomes opaque and black, accompanied by dissolution of the precipitate. The final solutions have red or blue opalescence. Components of the mixture may be separated by electrophoresis on polyacrylamide gels in tris–acetic acid buffer (pH 7.5).[16] With the exception of a small amount of red substance which does not permeate the gel, the product migrates toward the positive electode, and a series of blue and narrow red bands are developed. Their mobilities, dependent on the amino acid used, are reproducible. The relative intensities of the bands depend upon the amino acid and the handling of the sample. These properties show that $OsO_2(aa)_2$ complexes undergo secondary reactions, giving raise to other osmium–amino acid compounds, which are stable, anionic species of low molecular weight.

Molecular Structure of $OsO_2(NH_2CH_2COO)_2$. The data representing molecular parameters of the dioxobis(glycinato)osmium(VI) complex are given in Tables II–IV. The molecule belongs to the C_i point group and has a distorted pseudooctahedral structure (Figure 1). Two glycinato ($NH_2CH_2COO^-$) ligands coordinate through oxygen and nitrogen

(16) Manuscript in preparation.

Table VI. Selected Vibrational Frequencies for $OsO_2(aa)_2$ Complexes[a]

ligand						
gly	ala	val	leu	ile	phen	band assignt
3220 s	3185 s, br	3190 s, br	3190 s, br	3180 s, br	3175 s, br	NH_2 and N–H···O str
3100 s	3000 s, br	3150 s, br	3060 s, br	3140 s, br	3045 s, br	
3040 s		3090 s, br		3080 s, br		
2930 m	2920 w	2955 s	2940 s	2940 s	2900 sh	C–H str
	2900 w	2900 sh	2920 sh	2915 sh		
		2870 sh	2860 s	2860 s		
1665 s, br	1645 s, br	1640 s, br	1650 s, br	1630 s, br	1650 s, br	C=O asym str
1550 s, br	1575 s	1565 s, br	1580 s, br	1565 s, br	1590 sh	NH_2 scissors[b]
1510 sh	1560 s				1575 sh	
1405 m	1441 m	1455 m	1458 s	1444 m	1443 m	CH_2 scissors
850 s	850 s	861 s	855 s	855 s	850 s	O–Os–O str
610 m	603 s	595 s	595 s	596 s	588 s	CO_2 wag

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder. [b] Assignment based on the spectrum of N-deuterated glycinato complex.

with all four coordinating atoms and the osmium lying in a plane. The linear O–Os–O moiety is almost perpendicular to the defined plane with the oxygens being tilted by 0.3° toward the nitrogens. The distance between the apex oxygens and osmium of 1.73 Å is characteristic of a double bond[17] and the osmyl moiety. There is only a small decrease in C–C bond length with respect to zwitterionic glycine,[18] but a significant difference between the two carbon–oxygen distances in the carboxyl groups indicates considerable enhancement of C–O double bond character for the noncoordinating oxygen.

Within the crystal there are intermolecular hydrogen bonds between NH_2 groups and carbonyl oxygens. This is indicated by elongation of the N–H(1) bond. The intermolecular hydrogen–oxygen distances given in Table V show that additional weaker hydrogen bonds are present.

Infrared Spectra. The structural features of the six compounds can be verified on the basis of their infrared spectra. The assignments of diagnostic frequencies are given in Table VI. The region above 1400 cm^{-1} is almost identical for all the species independent of the amino acid. It also closely matches previously reported spectra of square-planar, bis(amino acidato) complexes of other transition metals.[19-23] The frequencies of the bands indicate, that the ligand coordinates through both nitrogen and oxygen[23] and that intermolecular hydrogen bonding exists.[19d]

In the region below 1400 cm^{-1} the important modes of NH_2, CO_2, Os–N, and Os–O should appear. In this region considerable similarity in spectra of various metal complexes with the same amino acid is observed. However, the assignments based on the analysis for the analogues of the osmyl compounds involving other metals did not provide fully justifiable and unequivocal results. The number and relative position of bands indicate that the above-mentioned modes undoubtedly appear. It is not possible to determine with confidence whether either one (asymmetric) or two Os–O and Os–N stretching modes are seen in the spectra. According to selection rules this information would discriminate between the possible cis and trans coordination of the nitrogen atoms.[22] By analogy to the glycinato species, one would expect the common trans geometry for all six osmyl compounds.

The strong band at 850 cm^{-1} is assigned to Os=O asymmetric stretch and is characteristic of the osmyl moiety.[24] In conclusion, the infrared spectra of the reported complexes are consistent with both classes of compounds they represent, namely, osmyl and square-planar amino acidato chelates. They indicate that the molecular structure of the glycinato complex is shared by all the compounds within this group.

Table VII. Crystallographic Data for $OsO_2(gly)_2$

formula	$C_4H_8N_2O_6Os$
mol wt	370.32
cryst dimens, mm	0.07 × 0.08 × 0.14
peak width at half-height, Å	0.15
radiation (Mo K$\bar{\alpha}$), Å	0.710 73
temp, °C	23 ± 1
space group	$P2_1/c$
cell dimens	
a, Å	5.041 (1)
b, Å	7.210 (2)
c, Å	10.885 (2)
β, deg	101.68 (1)
V, $Å^3$	387.4
Z	2
d_{calcd}, g/cm^3	3.17
μ, cm^{-1}	175.1

Experimental Section

Materials. The reagents used were supplied by the following companies: glycine, DL-alanine, DL-valine and DL-leucine by Mathenson, Colleman and Bell; DL-isoleucine and DL-phenylalanine by Eastman Kodak; 99.9% osminium tetroxide by Stevens Metalurigical Co.; 99.7% isotopic purity deuterium oxide by Merck and Co.

Preparation of Complexes. All compounds were routinely synthesized by mixing water solutions of amino acid and OsO_4. In a typical preparation 5 mL of amino acid solution (about 0.5 M glycine, alanine, and valine; the others close to saturation) was combined with 5 mL of 2% osmium tetroxide. Slowly precipitating solid was collected two or three times within several days by filtering off the liquid through a Buchner funnel. The precipitate was washed repeatedly with water and then with acetone. The time of some preparations was reduced to a few hours by heating the solution in a closed vial in a water bath at 50 °C. The typical yield was 80–150 mg. The N-deuterated

(17) Compare with data cited by J. M. Malin, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, **16**, 615 (1977) for Os=O of 1.75, 1.77, and 1.74 Å for $K_2[OsO_2Cl_4]$, $K_2[OsO_2(OH)_4]$, and $OsO_2(en)_2^{2+}$, respectively.

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Table VIII. Experimental Details of the Molecular Structure Determination of $OsO_2(gly)_2$

A. Intensity Measurements	
instrument	Enraf-Nonius CAD4 diffractometer
monochromator	graphite crystal, incident beam
attenuator	Zr foil, factor 20.7
takeoff angle	2.8°
detector aperture	2.0–2.8 mm horizontal, 2.0 mm vertical
cryst-to-detector dist	21 cm
scan type	ω–θ
scan rate	2–20°/min (in ω)
scan width	0.6 + 0.350 tan θ
max 2θ	80.0°
no. of reflctns measd	2613 total, 2381 unique
corrections	lorentz-polarization, linear decay (from 1.000 to 1.023 on I), extinction (coefficient = 0.000 001 6), empirical absorption (from 0.63 to 1.00 on I)
B. Structure Solution and Refinement	
solution	Patterson method
hydrogen atoms	located and refined isotropically
refinement	full-matrix least-squares
minimization function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
"ignorance" factor	0.030
anomalous dispersion	all nonhydrogen atoms
reflctns included	1441 with $F_o^2 > 3.0\sigma(F_o^2)$
parameters refined	78
unweighted agreement factor	0.022
weighted agreement factor	0.028
factor including unobserved reflctns	0.051
esd of observation of unit weight	1.21
convergence, largest shift	0.01σ
highest peak in final difference Fourier	1.8 (1) e/A (near Os atom)
computer hardware	linked PDP-11/45-11/60
computer software	Enraf-Nonius SDP and private programs of Molecular Structure Corp.

complex of glycine was prepared as above by using D_2O as a solvent. A similar procedure for alanine gave a product containing mainly nondeuterated species.

Analysis. C, H, and N analyses were carried out by Galbraith Laboratories. The content of osmium was determined spectrophotometrically by oxidation to OsO_4, formation of the thiourea complex, and an absorption measurement at λ = 480 nm.[25] Serious difficulties in dissolving samples and quantitative oxidation to OsO_4 were initially encountered. The developed procedure involved dissolution of a sample (5–20 mg) in 18 M H_2SO_4 (0.5–1 mL). After 1–2 h, the solution was transferred to 50- or 100-mL volumetric flask, and reagents were added in the following sequence: 2–3 mL of 40% NaOH, 2–3 mL of 0.2–0.5 M $KMnO_4$ (solution turns green), 5–10 mL of 6 N H_2SO_4 (red solution), 1–2 drops of 30% H_2O_2 (solution discolored), and 10 mL of 2 N thiourea. The flask was filled to the mark with distilled water and the absorption measured. Os content was calculated from the calibration line: [μg of Os/mL] = (A - 0.002)/0.0222.

Molecular Structure. The structure of the $OsO_2(gly)_2$ species has been determined by the crystallographic staff of Molecular Structure Corp., College Station, TX.[26] Crystals were prepared according to the procedure described above and submitted to the company. Tables VII and VIII listing details of the determination are taken from the report received.

Infrared Spectra. The spectra of KBr pellets containing 2–3 mg of a sample were taken on Perkin-Elmer Model 225 spectrophotometer from 300 to 4000 cm^{-1}. Positions of sharp bands were determined from instrument readings. Pellets darkened in the course of measurement and finally turned opaque black. It was found, by starting a measurement with a fresh pellet at different points of the region studied, that most of the bands were not affected by these changes in the pellet appearance. However, it is not known whether some very weak bands and "shoulders" were associated with the darkening or constituted a part of the spectrum of investigated complex. The use of a cold-air blower slowed down the process but did not prevent it.

Acknowledgment. This research was supported by the Department of Chemistry and Biochemistry, the Molecular Science Program, and the Office of Research Development and Administration of Southern Illinois University. A gift of OsO_4 from Mallinkrodt, Inc., is gratefully acknowledged.

Registry No. $OsO_2(gly)_2$, 77153-90-3; $OsO_2(ala)_2$, 77153-89-0; $OsO_2(val)_2$, 77153-88-9; $OsO_2(leu)_2$, 77153-87-8; $OsO_2(ile)_2$, 77153-86-7; $OsO_2(phe)_2$, 77153-85-6; OsO_4, 20816-12-0.

Supplementary Material Available: Report on molecular structure determination of $OsO_2(gly)_2$ as received from the Molecular Structure Corp., which includes the description of experimental procedures, tables of general temperature factor expressions, root-mean-square amplitudes of thermal vibration, torsional angles, intermolecular contacts up to 3.5 Å, and least-squares planes and intensity data, and infrared spectra of the complexes (22 pages). Ordering information is given on any current masthead page.

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