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Synthesis and X-ray Structure of the Unusual Cysteine-Complex $OsH_2\{OC(=O)CH[NHC(=O)CH_3]CH_2S\}(P^iPr_3)_2$

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The biological importance of metal−cysteine interactions has been a relevant factor in the development of the coordination chemistry of cysteine and related molecules.[1] Thus, several main group and transition metal complexes containing cysteine and cysteine derivatives have been synthesized in recent years.[2]

The importance of cysteine in biological systems has been ascribed to the chemical properties of the thiol group, which can undergo acid−base and oxidation−reduction reactions.[3] High oxidation state metal complexes of cysteine are usually difficult to prepare due to the facile oxidation of cysteine by oxidized metal ions. Here we report a high oxidation state metal−cysteine complex, which is the first example of a dihydrido compound of this type.

Recently, we have shown that the reactions of $IrH_5(PPh_3)_2$ with carboxylic acids give $IrH_2(\eta^2\text{-}O_2CR)(PPh_3)_2$ and molecular hydrogen.[4] Continuing our work on the reactivity of transition metal polyhydrido complexes toward organic acids, we have now carried out the reaction of the hexahydrido $OsH_6(P^iPr_3)_2$ (**1**) with *N*-acetyl-L-cysteine ($HSCH_2\{CH_3C(=O)NH\}CHCO_2H$ (**2**)). Thus, the treatment of **1** with **2** in a 1:1 molar ratio, in toluene at 110 °C, gives a red solution from which the complex $OsH_2\{OC(=O)CH[NHC(=O)CH_3]CH_2S\}(P^iPr_3)_2$ (**3**) is separated by addition of hexane, as a brown solid in 82% yield.

An X-ray diffraction experiment carried out on a single crystal of **3** indicates that the structure has two independent molecules in the asymmetric unit. ORTEP diagrams of both molecules are shown in Figure 1.

The geometry around the metal center in both molecules (**a** and **b**) could be ideally described as derived from a distorted square antiprism with two vacant coordination sites (Figure 2). One of the two square-planes is made up by two phosphorus atoms and the two hydrido ligands,[5] which occupy alternate positions. The sulfur atom and the coordinated oxygen of the *N*-acetyl-L-cysteinato ligand are located in the second plane, which is rotated by 38.9(2)° from the first one, in the molecule **a**, and 46.6(2)° in the molecule **b**. For the related complex $OsH_2Cl_2(P^iPr_3)_2$, a similar structure has been recently reported by us.[7]

The unusual geometry around the osmium atoms of the molecules **a** and **b** should be noted. Although, *N*-acetyl-L-cysteinato can act as a tridentate (N, O, S) ligand, the complex **3** is an unsaturated compound.[2g,8] This could indicate that the coordination polyhedron determined by the donor atoms of **3** and those of $OsH_2Cl_2(P^iPr_3)_2$ is an intrinsic salient feature for dihydridoosmium(IV) complexes containing bulky phosphine ligands.

For cysteine, the bidentate (O, S) coordination is rare. To the best of our knowledge, the only cysteine transition metal complex with bidentate (O, S) coordination, previously characterized by X-ray diffraction analysis, is the nitridoosmium(VI) complex $[N^nBu_4][Os(N)\{OC(=O)CH[NHC(=O)CH_3]CH_2S\}_2]$. This compound has been obtained by Shapley and co-workers[2h] from the reaction of *N*-acetyl-L-cysteine and $[N^nBu_4][Os(N)Cl_4]$ in the presence of Et_3N. In this pentacoordinated Os(VI) complex (92.2 and 91.1(3)°) as in **3** (89.4 and 89.6(3)°) the bite angles of the (O,S)-bidentate cysteine ligand are very similar with values close to 90°.

The molecules **a** and **b** of **3** have no symmetry elements other than a C_1 axis. As a consequence the metal centers are chiral in the solid state. However, since there is an asymmetric center on the *N*-acetyl-L-cysteinato ligands, both independent molecules, **a** and **b**, could be described as diastereoisomers. At first glance, the only difference between them, apart of the conformations of the metallacycle ring, is the disposition around the metal of the *N*-acetyl-L-cysteinato. This ligand occupies in one diastereoisomer positions corresponding to the vacant coordination sites of the other diastereoisomer (Figure 2). In agreement with the presence of two diastereoisomers in the crystal structure of **3**, the IR spectrum of this compound in Nujol shows four ν(Os−H) bands at 2200, 2180, 2135 and 2080 cm^{-1}.

On the other hand, complex **3** has not a rigid structure in solution, even at −90 °C. Thus, the ^1H and $^{31}P\{^1H\}$ NMR spectra of **3** are temperature dependent (Figure 3). At room temperature the ^1H NMR spectrum contains in the hydrido region a triplet at −15.96 ppm with a P−H coupling constant of 36.5 Hz. At the same temperature the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 39.60 ppm, that under off-resonance conditions due to P−H coupling is split into a triplet. At −90 °C, the ^1H NMR spectrum has in the high field region three broad resonances at −15.2, −17.0, and −17.9 ppm, whereas, the $^{31}P\{^1H\}$ NMR spectrum shows two AB systems between 55 and 25 ppm as it was expected from the X-ray structure. The spectra shown in Figure 3 suggest that in solution the molecule **a** is readily converted into **b** (or **b** into **a**).

In summary, the reaction of the hexahydrido $OsH_6(P^iPr_3)_2$ with *N*-acetyl-L-cysteine affords $OsH_2\{OC(=O)CH[NHC(=O)CH_3]CH_2S\}(P^iPr_3)_2$, which crystallizes as two diastereoisomers containing the *N*-acetyl-L-cysteinato ligand with bidentate (O, S) coordination. Interestingly, the coordination

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(5) The final electronic residuals of the X-ray analysis showed the presence of two peaks in each independent molecule assignable to the hydride ligands. Unfortunately a proper free refinement of these atoms was not successful. As these positions geometrically agree well with those calculated from electrostatic potentials,[6] the latter have been included in the description of the structure.

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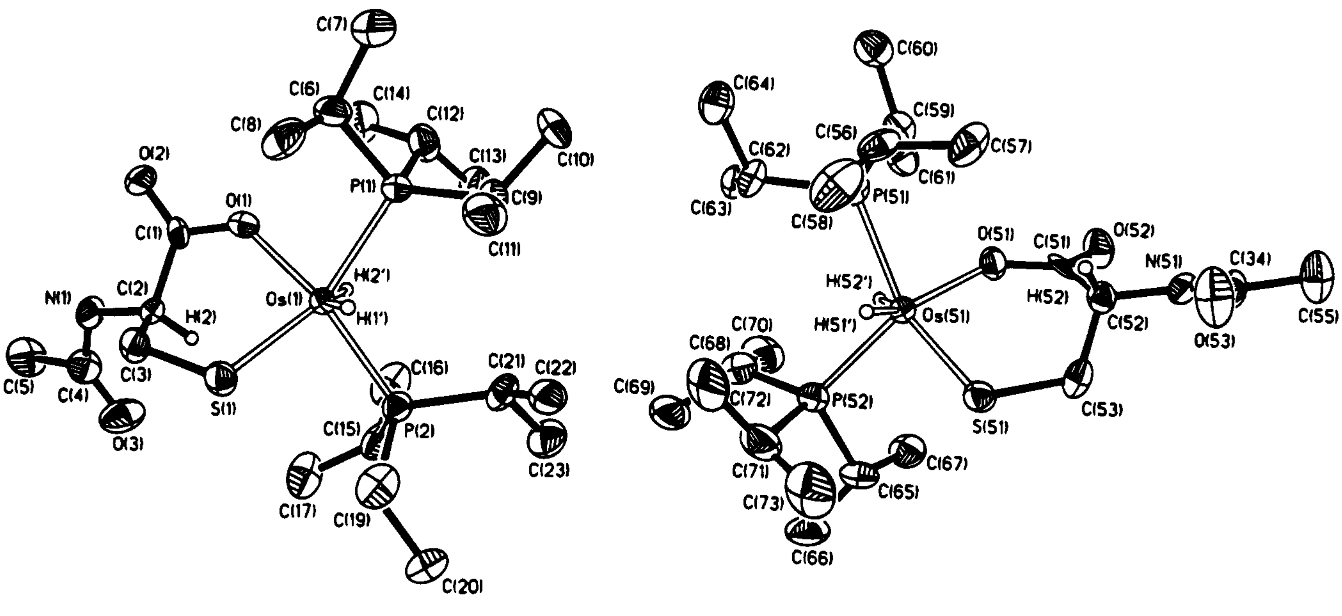

(a) **(b)**

Figure 1. Molecular diagrams for the two independent molecules (**a** and **b**) of complex **3**. The hydride calculated positions have also been included to ease the metal coordination description.

Table 1. Selected Bond Distances (Å) and Angles (degree) for **3**[a]

	molecule			molecule	
	a	**b**		**a**	**b**
Os(1)−P(1)	2.348(4)	2.331(4)	Os(1)−P(2)	2.291(4)	2.295(4)
Os(1)−S(1)	2.314(4)	2.298(4)	Os(1)−O(1)	2.097(10)	2.080(8)
S(1)−C(3)	1.826(15)	1.803(15)	O(1)−C(1)	1.293(17)	1.299(17)
C(2)−C(3)	1.493(21)	1.520(21)	C(1)−C(2)	1.506(19)	1.556(21)
P(1)−Os(1)−P(2)	112.2(1)	112.9(1)	P(1)−Os(1)−H(1′)	78.6	77.9
P(1)−Os(1)−S(1)	146.3(1)	141.8(1)	P(1)−Os(1)−H(2′)	82.0	83.0
P(1)−Os(1)−O(1)	82.0(3)	87.4(3)	P(2)−Os(1)−H(1′)	87.0	81.5
P(2)−Os(1)−S(1)	91.4(1)	91.3(1)	P(2)−Os(1)−H(2′)	79.2	76.4
P(2)−Os(1)−O(1)	149.5(3)	143.6(3)	S(1)−Os(1)−H(1′)	79.1	77.1
S(1)−Os(1)−O(1)	89.4(3)	89.6(3)	S(1)−Os(1)−H(2′)	127.5	132.9
H(1′)−Os(1)−H(2′)[b]	149.8	142.3	O(1)−Os(1)−H(1′)	123.0	133.9
O(1)−Os(1)−H(2′)	76.3	76.5			

[a] The labeling scheme used in the table corresponds to that of molecule **a**, while that used for molecule **b** relates to this by adding 50 to the number of each atom. [b] The hydride positions were estimated from electrostatic potential energy calculations (Os−H = 1.66 Å).

Table 2. Crystallographic Data for **3**

formula	$C_{23}H_{51}NO_3OsP_2S$	space group	$P2_12_12_1$
fw	673.87	V (Å^3)	5986.1(6)
a (Å)	14.463(1)	Z	8
b (Å)	18.051(1)	T (K)	233
c (Å)	22.929(1)	λ (Å)	0.710 69
R^a	0.0538	ϱ (g·cm^{-3})	1.495
$R_w{}^b$	0.0569	μ(Mo $K\alpha$) (cm^{-1})	44.56

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R_w = [\Sigma w^{1/2}|F_o - F_c|/\Sigma w^{1/2}|F_o|]$.

polyhedron for both diastereoisomers, is similar to that previously observed for the complex $OsH_2Cl_2(P^iPr_3)_2$, and can be described as a square antiprism with two vacant coordination sites. This geometry could be an intrinsic salient feature for dihydridoosmium(IV) complexes containing bulky phosphines.

Experimental Section

The reaction was carried out with rigorous exclusion of air by using Schlenk tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. The starting complex $OsH_6(P^i\text{-}Pr_3)_2$ (**1**) was prepared by a published method.[7]

NMR spectra were recorded on a Varian UNITY 300 spectrophotometer. Chemical shifts are expressed in ppm from Me_4Si (^1H) and

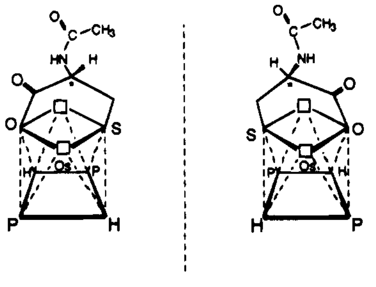

Figure 2. Ideal representation of the coordination polyhedra of the isomers **a** and **b** of complex **3**.

85% H_3PO_4 (^{31}P). Infrared spectra were recorded with a Perkin-Elmer 783 spectrophotometer. C and H analysis were carried out on a Perkin-Elmer 240C microanalyser.

Preparation of $OsH_2\{OC(=O)CH[NHC(=O)CH_3]CH_2S\}(P^iPr_3)_2$ (3). A solution of $OsH_6(P^iPr_3)_2$ (177.0 mg, 0.35 mmol) in 10 mL of toluene was treated with *N*-acetyl-L-cysteine (57.0 mg, 0.35 mmol). After being stirred for 15 min at 110 °C, the solution was filtered through diatomaceous earth. The red filtrate was concentrated to *ca.* 0.1 mL; addition of hexane caused the precipitation of a brown solid. The solvent was decanted, and the solid was washed twice with hexane and then dried in vacuo. Yield: 93 mg (80%). Anal. Calcd for C_{23}-

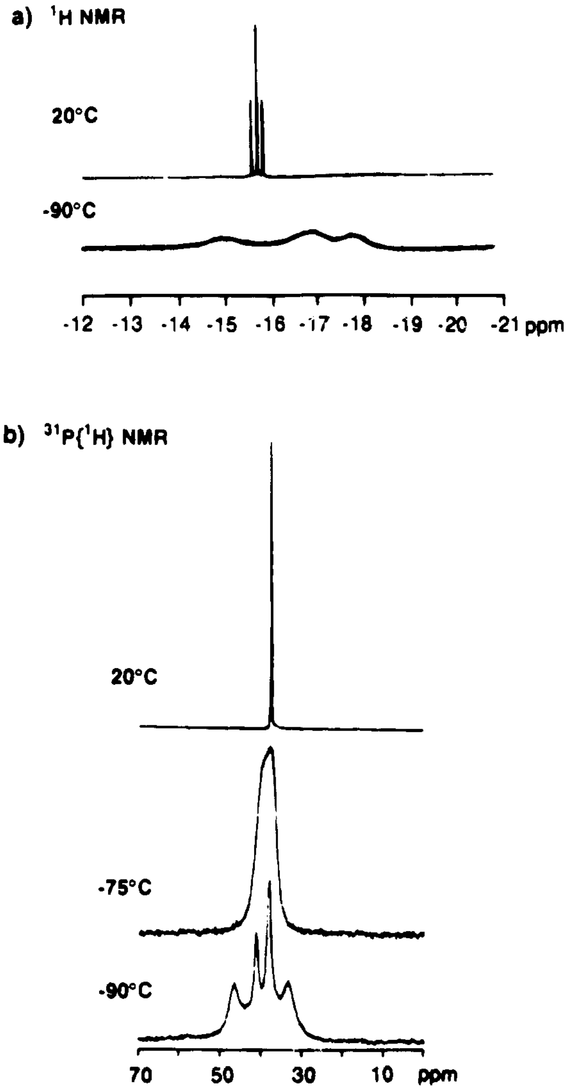

Figure 3. (a) ^{1}H NMR (toluene-d_8) spectrum of **3** in the hydrido region as a function of temperature. (b) ^{31}P{^{1}H} NMR (toluene-d_8) spectrum of **3** as a function of temperature.

$H_{51}NO_3OsP_2S$: C, 40.99; H, 7.64; N, 2.08. Found: C, 41.38; H, 8.35; N, 2.04. IR(Nujol): ν(NH) 3295; ν(OsH) 2200, 2180, 2135, 2080; ν(C=O) 1665, 1620 cm^{-1}. ^{1}H NMR (300 MHz, toluene-d_8, room temperature): δ 6.88 (d, J(HH) = 4.8 Hz, 1H, NH), 4.37 (dd, J(HH) = 3.3 and 12.3 Hz, 1H, $-CH_2S$), 4.25 (ddd, J(HH) = 3.3, 4.8 and 12.1 Hz, 1H, OC(=O)CH−), 2.6 (t, J(HH) = 12.2 Hz, 1H, $-CH_2S$), 2.29 (m, 6H, PCH−), 1.94 (s, 3H, $CH_3-C(=O)-$), 1.29 (dd, J(PH) = 7.1, J(HH) = 3.4 Hz, 18H, PCH−CH_3), 1.24 (dd, J(PH) = 7.0, J(HH) = 3.3 Hz, 18H, PCH−CH_3), −15.96 (t, J(PH) = 36.5 Hz, 2H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, toluene-d_8, room temperature): δ 39.60 (s; t under off-resonance conditions).

X-ray Structure Analysis of 3. Crystals suitable for the X-ray diffraction experiment were obtained by slow diffusion of hexane into a concentrated solution of **3** in toluene. Table 2 collects some relevant crystallographic data. A total of 9579 reflections were measured ($3 \le 2\theta \leqslant 47°$) on a four-circle Siemens-Stoe AED diffractometer. Intensity data were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitorized every 55 min of measuring time; no variation was observed. Absorption correction was also applied by an empirical method.[9] Of 8836 unique reflections, 8145 which had $F_o \ge 4.0\sigma(F_o)$ were used in the structure analysis.

The crystal structure was solved by using the heavy atom method followed by conventional Fourier techniques and subsequent least-squares refinement. All atoms but the hydrogen ones were refined anisotropically. The hydrogen atoms, except hydrides, were included in the last cycles of refinement and refined riding on carbon or nitrogen atoms with a common thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Os, P, and S were taken from ref 10. All calculations were performed by use of the SHELXTL-PLUS system.[11]

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Supplementary Material Available: Tables of atomic coordinates, anisotropic displacement parameters, hydrogen atom coordinates, experimental details of the X-ray study, and bond distances and angles (22 pages). Ordering information is given on any current masthead page.

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