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Synthesis, X-ray Characterization, and Reactivity of α-Aminoacidato Ethoxide Complexes of Niobium(V) and Tantalum(V)

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Supporting Information

ABSTRACT: High yields of the ethoxo-α-aminoacidates of the general formula $M(OEt)_4[OC(O)CHRNHR'\text{-}\kappa O,\kappa N]$ (M = Nb, R = CH_2Ph, R′ = H, **2**; R = $CHMe_2$, R′ = H, **3**; R = CH_2CHMe_2, R′ = H, **4**; R = H, R′ = Me, **5**; R = CH_2CH_2SMe, R′ = H, **6**; M = Ta, R = CH_2Ph, R′ = H, **7**; R = CH_2CH_2SMe, R′ = H, **8**) and $M(OEt)_4(OC(O)CH(CH_2CH_2CH_2)NH\text{-}\kappa O,\kappa N)$ (M = Nb, **9**; Ta, **10**) have been obtained by the reaction of the L-enantiopure α-amino acid (or sarcosine) with a slight molar excess of $M(OEt)_5$ (M = Nb, **1a**; Ta, **1b**) in a dichloromethane solution. The new complexes **2**−**10** have been fully characterized by spectroscopic and analytical methods and by X-ray diffraction for **2** and **7**−**9**. Such X-ray structures are the first ones ever reported for niobium and tantalum coordination compounds containing an α-aminoacidato ligand. The early−late heterobimetallic derivative $Ta(OEt)_4[O_2CCH(NH_2)CH_2CH_2S(CH_3)(AuCl)]$ (**11**) has been prepared by the reaction of **8** with a stoichiometric amount of Au(CO)Cl. The bulk polymerization of D,L-lactide initiated by complexes **2** and **7** gave a slightly heterotactic enchainment (P_r = 0.54 and 0.63, respectively), whereas complexes **1a** and **1b** formed fully atactic polylactide with $P_r \approx 0.4$.

■ INTRODUCTION

The chemistry of metal alkoxides, which dates back more than 100 years, has received growing attention by a number of research groups during the past decade.[1] In particular, group 5 metal alkoxides, especially those of niobium and tantalum, have been studied so far because of their potential applications in chemical vapor deposition[2] and catalysis[3] and as precursors of M_2O_5 nanospheres,[4] nanorods,[5] microporous membranes,[6] and electrooptic and ceramic materials.[7] Moreover, niobium and tantalum alkoxides have been widely used as starting materials for the preparation of a variety of organometallic and coordination compounds.[8−10]

Our recent interest in the chemistry of oxygen-donor species with niobium and tantalum derivatives,[11] consisting in the preparation and study of the reactivity of new systems that might find use as catalytic precursors, prompted us to examine the reactivity of $M(OEt)_5$ (M = Nb, **1a**; M = Ta, **1b**)[12] with natural α-amino acids. In fact, aminoacidato derivatives of early transition metals have proven to exhibit interesting properties in very different fields such as asymmetric synthesis in organic media[13] and in aqueous solution,[13b] cytotoxicity,[14] sol−gel-derived coatings,[15] and bioorganometallic[16] and solid-state chemistry.[17]

On the other hand, studies on the interactions of niobium and tantalum species with amino acids are surprisingly rare. An IR investigation on a niobium(V) aqueous system was reported;[18] however, the only example of a well-defined coordination compound is, to the best of our knowledge, a cyclopentadienylalaninato derivative of tantalum(V).[19] Niobium/tantalum salts (e.g., phosphates) incorporating interlayer amino acids have been described.[20] It is remarkable that the modification of niobium alloy surfaces by the addition of short amino acid sequences has proven to confer excellent resistance properties to the materials employed for surgical implants.[21]

We present herein the preparation of the first, fully characterized coordination complexes of niobium and tantalum containing α-aminoacidato ligands, together with the synthesis of a rare example of tantalum−gold heterobimetallic species, bearing a bridged methionato ligand. Furthermore, the lactide (LA) polymerization behavior of the newly prepared phenylalaninato complexes will be discussed.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed under an atmosphere of prepurified argon using standard Schlenk techniques. The reaction vessels were oven-dried at 150 °C prior to use, evacuated (10^{-2} mmHg), and then filled with argon. $M(OEt)_5$ (M = Nb, **1a**, 99.9+%; M = Ta, **1b**, 99.99+%) were purchased from Strem and stored under an argon atmosphere as received. L-Phenylalanine (PheH), L-valine (ValH), L-leucine (LeuH), L-proline (ProH) (Apollo Scientific), sarcosine (SarH), L-methionine (MetH), and L-lactide and D,L-lactide (Sigma-Aldrich) were commercial products of the highest purity available, stored under an argon atmosphere as received. Au(CO)Cl was prepared from $AuCl_3$, CO, and $SOCl_2$ according to the literature.[22] Solvents (Sigma Aldrich) were distilled from the appropriate drying agents under an argon atmosphere before use:

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CH_2Cl_2, CD_2Cl_2, and $CDCl_3$ from P_4O_{10}, toluene from sodium, and hexane and heptane from $LiAlH_4$. IR spectra were recorded at 298 K on a Perkin-Elmer FT-IR spectrometer, equipped with an UATR sampling accessory. NMR spectra were recorded at 298 K on a Bruker Avance DRX400 instrument equipped with a BBFO broad-band probe. The chemical shifts for ^1H and ^{13}C were referenced to the nondeuterated aliquot of the solvent, while the chemical shifts for ^{93}Nb were referenced to external $[NEt_4][NbCl_6]$. The ^1H and ^{13}C NMR spectra were fully assigned via $^1H-^{13}C$ correlation measured through gs-HSQC and gs-HMBC experiments.[23] NMR signals attributed to a second isomeric form (where it has been possible to detect them) are italicized. Carbon, hydrogen, and nitrogen analyses were performed on a Carlo Erba model 1106 instrument. The chloride content of **11** was determined by the Mohr method[24] on a solution prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and the addition of HNO_3 up to neutralization. The metal (M = Nb, Ta) was analyzed as M_2O_5, obtained by hydrolysis of the sample, followed by calcination in a platinum crucible. The gas-volumetric measurements were performed with the apparatus described by Calderazzo and Cotton.[25] Molecular weights of polymers were determined by size-exclusion chromatography (SEC), using chloroform as the eluent (1 mL/min), a high-performance liquid chromatography pump equipped with a 50 μm Rheodyne loop, a Waters 515 oven at 35 °C, a Waters 2410 refractive index detector, and a PL 5-μm gel MIXED-C column. Monodispersed polystyrene standards were employed for calibration of the columns.

1. General Synthesis of $M(OEt)_4$(amino acidato) Complexes. The synthesis of compound **2** is described in detail; compounds **3**−**10** were obtained by analogous procedures.

The syntheses of **2**, **3**, **6**, and **10** were performed also in CD_2Cl_2 (ca. 0.8 mL) in an NMR tube, by allowing $M(OEt)_5$ (0.20 mmol) to react with the appropriate aminoacid (0.20 mmol) in the presence of $CHCl_3$ (0.20 mmol) used as the standard. NMR analyses performed at the end of the reactions showed the presence of EtOH ($EtOH/CHCl_3$ ratio = 1) in all cases.

*$Nb(OEt)_4[OC(O)CH(CH_2Ph)NH_2$-κO,κN] (**2**).* A suspension of PheH (0.119 g, 0.720 mmol) in CH_2Cl_2 (15 mL) was treated with $Nb(OEt)_5$ and **1a** (0.200 mL, 0.797 mmol). The resulting mixture was stirred at room temperature for 18 h; thus, a colorless solution was obtained. The solution was concentrated up to 3 mL and layered with hexane. Colorless crystals of **2** were collected after 48 h. Yield: 0.266 g, 85%. The reaction of PheH (0.396 g, 2.40 mmol) with **1a** (0.600 mL, 2.40 mmol) was carried out in $CHCl_3$ at reflux temperature for 18 h: the product **2** was isolated in 73% yield (0.762 g). Anal. Calcd for $C_{17}H_{30}NNbO_6$: C, 46.69; H, 6.91; N, 3.20; Nb, 21.24. Found: C, 46.32; H, 6.49; N, 3.37; Nb, 20.89. IR (solid state): 3291w, 3217w, 3058w, 2966w-m, 2866w-m, 1648s, 1605w-m, 1498w-m, 1452w, 1438w, 1377m-s, 1349w, 1328w, 1257m, 1216w, 1098s, 1055s, 908s, 877w-m, 828w-sh, 796m, 753m, 701m-s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.39−7.30 (5 H, C_6H_5); 4.37, 4.21 (m, 8 H, OCH_2); 3.92 (m, 1 H, NCH); 3.28 (m, 2 H, CH_2Ph); 2.97, 2.55 (m, 2 H, NH_2); 1.23 (m-br, 12 H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 176.0 (CO); 136.2 (*ipso*-Ph); 129.7, 129.3, 127.6 (C_6H_5); 71.8, 67.5 (OCH_2CH_3); 58.6 (NCH); 39.1 (CH_2Ph); 18.4 (OCH_2CH_3). ^{93}Nb NMR ($CDCl_3$): δ −1201 ($\Delta\nu_{1/2}$ = 1.1 × 10^4 Hz).

*$Nb(OEt)_4[OC(O)CH(CHMe_2)NH_2$-κO,κN] (**3**):* colorless solid, 0.291 g and 86% yield from **1a** (0.250 mL, 1.00 mmol) and ValH (0.117 g, 1.00 mmol). Anal. Calcd for $C_{13}H_{30}NNbO_6$: C, 40.11; H, 7.77; N, 3.60; Nb, 23.87. Found: C, 40.14; H, 7.88; N, 3.52; Nb, 23.60. IR (solid state): 3226m-br, 3134m-br, 2966w-m, 2927w, 2864w-m, 1653s, 1606w-sh, 1560w, 1468w, 1441w, 1375m-s, 1336w, 1308w, 1259m-s, 1059m-s, 1049s, 908vs, 792vs, 724w-m, 662w cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.48, 4.25 (m, 8 H, OCH_2); 3.69 (m, 1 H, NCH); 3.56, 2.57 (br, 2 H, NH_2); 2.68 (m, 1 H, $CHCH_3$); 1.28 (m-br, 12 H, OCH_2CH_3); 1.06, 0.94 (m, 6 H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 176.3 (CO); 68.7, 67.9, 67.3 (OCH_2CH_3); 63.3 (NCH); 30.1 ($CHCH_3$); 19.3, 15.8 ($CHCH_3$); 18.7, 18.2 (OCH_2CH_3). ^{93}Nb NMR ($CDCl_3$): δ −1180 ($\Delta\nu_{1/2}$ = 2.0 × 10^4 Hz).

*$Nb(OEt)_4[OC(O)CH(CH_2CHMe_2)NH_2$-κO,κN] (**4**):* colorless solid, 0.319 g and 88% yield from **1a** (0.25 mL, 1.00 mmol) and LeuH (0.118 g, 0.90 mmol). Anal. Calcd for $C_{14}H_{32}NNbO_6$: C, 41.69; H, 8.00; N, 3.47; Nb, 23.04. Found: C, 41.23; H, 8.50; N, 3.33; Nb, 23.20. IR (solid state): 3245m-br, 3153w-m, 2967w-m, 2922w, 2866w-m, 1650vs, 1619w-sh, 1469w, 1442w, 1372m-s, 1331m-s, 1309w, 1273w, 1261w, 1245w, 1126w, 1097s, 1044vs, 984w, 904vs, 834w-m, 799w-m, 770w-m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.27 (q, $^3J_{HH}$ = 6.97 Hz, 6 H, OCH_2); 4.05 (q, $^3J_{HH}$ = 6.60 Hz, 2 H, OCH_2); 3.46 (m, 1 H, $CHNH_2$); 3.04 (br, 1 H, NH), 2.38 (m, 1 H, NH); 1.81, 1.35 (m, 2 H, $CHCH_2$), 1.64 (s, 1 H, $CHCH_3$); 1.04 (m, 12 H, OCH_2CH_3); 0.80, 0.77 (m, 6 H, $CHCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 178.3 (CO); 71.5, 68.7, 67.0 (OCH_2CH_3); 56.0 ($CHNH_2$); 43.3 ($CHCH_2$); 24.7 ($CHCH_3$); 23.2, 20.8 ($CHCH_3$); 18.6, 18.2, 17.5 (OCH_2CH_3). ^{93}Nb ($CDCl_3$): δ −1154 ($\Delta\nu_{1/2}$ = 2.0 × 10^4 Hz).

*$Nb(OEt)_4[OC(O)CH_2NHMe$-κO,κN] (**5**):* colorless solid, 0.191 g and 74% yield from **1a** (0.200 mL, 0.797 mmol) and SarH (0.064 g, 0.717 mmol). Anal. Calcd for $C_{11}H_{26}NNbO_6$: C, 36.57; H, 7.25; N, 3.88; Nb, 25.72. Found: C, 36.12; H, 7.41; N, 3.63; Nb, 25.54. IR (solid state): 3140m-br, 2970w-m, 2925w, 2865w-m, 1655vs, 1577w-sh, 1469w, 1441w, 1354s, 1317m, 1261w-m, 1144w-sh, 1096s, 1049vs, 968m, 910s, 798m-s, 722m, 661w cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.47, 4.24 (m, 8 H, OCH_2); 3.85 (br, 2 H, NCH_2); 3.14 (br, 1 H, NH); 2.59, *2.48* (s, 3 H, NCH_3); 1.24 (m, 12 H, OCH_2CH_3). Isomer ratio 8:1. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 174.9 (CO); 68.8, 67.9 (OCH_2CH_3); 57.4, *54.6* (NCH_2); 38.8, *36.1* (NCH_3); 18.7, 18.3, 17.6 (OCH_2CH_3). ^{93}Nb (CD_2Cl_2): δ −1195 ($\Delta\nu_{1/2}$ = 1.0 × 10^4 Hz).

*$Nb(OEt)_4[OC(O)CH(CH_2CH_2SMe)NH_2$-κO,κN] (**6**):* colorless solid, 0.255 g and 84% yield from **1a** (0.200 mL, 0.797 mmol) and MetH (0.107 g, 0.721 mmol). Anal. Calcd for $C_{13}H_{30}NNbO_6S$: C, 37.06; H, 7.18; N, 3.32; Nb, 22.05. Found: C, 36.80; H, 7.11; N, 3.60; Nb, 22.21. IR (solid state): 3234m-br, 3127m-br, 2968w-m, 2917w, 2861w-m, 1651s, 1590w-sh, 1469w, 1441w, 1375m-s, 1333m, 1295w, 1260m-s, 1136w, 1094s, 1041vs, 903s, 795s, 735w, 663w cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.45, 4.21 (m, 8 H, OCH_2); 3.80 (m, 1 H, NCH); 3.14, 2.64 (m, 2 H, NH_2); 2.74 (m, 2 H, SCH_2); 2.38, 1.97 (m, 2 H, SCH_2CH_2); 2.12 (s, 3 H, SCH_3); 1.27, 1.22 (m, 12 H, OCH_2CH_3). Isomer ratio ca. 1.1: 1. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 177.2 (CO); 71.3, 68.7, 67.8, 67.2 (OCH_2CH_3); 57.1 (NCH); 32.3 (SCH_2CH_2); 30.6 (SCH_2); 18.6, 18.2, 17.5 (OCH_2CH_3); 14.8 (SCH_3). ^{93}Nb (CD_2Cl_2): δ −1194 ($\Delta\nu_{1/2}$ = 1.3 × 10^4 Hz).

*$Ta(OEt)_4[OC(O)CH(CH_2Ph)NH_2$-κO,κN], **7**.* Colorless solid, 0.302 g, 79% yield from **1b** (0.210 mL, 0.810 mmol) and PheH (0.120 g, 0.730 mmol). Crystals suitable for X-ray analysis were collected from CH_2Cl_2/hexane at −30 °C. Anal. Calcd for $C_{17}H_{30}NO_6Ta$: C, 38.86; H, 5.76; N, 2.67; Ta, 34.44. Found: C, 38.70; H, 5.91; N, 2.49; Ta, 34.31. IR (solid state): 3286w, 3214w, 3088w-m, 2975 w-m, 2864 w-m, 1661s, 1606w-m, 1496w, 1441w, 1380m-s, 1350w-m, 1330w-m, 1260m, 1215w, 1196w, 1143w-m, 1105s, 1062s, 912s, 883m, 826w-m, 758s, 706s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.37−7.29 (5 H, C_6H_5); 4.49, 4.39 (m, 8 H, OCH_2); 3.98 (m, 1 H, NCH); 3.29 (m, 2 H, CH_2Ph); 3.15, 2.68 (m, 2 H, NH_2); 1.23 (m-br, 12 H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.5 (CO); 136.0 (*ipso*-Ph); 129.7, 129.3, 127.7 (C_6H_5); 69.8, 66.5 (OCH_2CH_3); 58.5 (NCH); 39.1 (CH_2Ph); 19.2, 18.8 (OCH_2CH_3).

*$Ta(OEt)_4[OC(O)CH(CH_2CH_2SMe)NH_2$-κO,κN] (**8**):* colorless solid, 0.331 g and 80% yield from **1b** (0.23 mL, 0.900 mmol) and MetH (0.121 g, 0.813 mmol). Crystals suitable for X-ray analysis were collected from toluene/heptane at room temperature. Anal. Calcd for $C_{13}H_{30}NO_6STa$: C, 30.65; H, 5.94; N, 2.75; Ta, 35.52. Found: C, 30.80; H, 5.86; N, 2.74; Ta, 35.11. IR (solid state): 3220m-br, 3123m-br, 2968w-m, 2919w, 2864w-m, 1661s, 1621w-sh, 1593w, 1473w, 1441w-m, 1377m-s, 1333m, 1296w, 1260m-s, 1146w, 1098s, 1051vs, 903vs, 879w-sh, 798s, 675w cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.62, 4.33 (m, 8 H, OCH_2); 3.91 (m, 1 H, NCH); 3.25, 2.40 (br, 2 H, NH_2); 2.66 (m, 2 H, SCH_2); 2.55, 2.03 (m, 2 H, SCH_2CH_2); 2.12 (s, 3 H, SCH_3); 1.32 (m, 12 H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 175.9 (CO); 71.6, 69.2 (OCH_2CH_3); 57.1 (NCH); 32.6 (SCH_2CH_2); 30.9 (SCH_2); 18.1 (OCH_2CH_3); 14.8 (SCH_3).

Table 1. Crystal Data and Experimental Details for **2** and **7**−**9**

	2	7	8	9
formula	$C_{17}H_{30}NNbO_6$	$C_{17}H_{30}NO_6Ta$	$C_{13}H_{30}NO_6STa$	$C_{13}H_{28}NNbO_6$
fw	437.33	525.37	509.39	387.27
T, K	100(2)	100(2)	100(2)	100(2)
cryst syst	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
a, Å	7.4524(15)	7.4724(12)	15.465(3)	10.2162(18)
b, Å	11.282(2)	11.2720(18)	10.1091(19)	10.5175(19)
c, Å	23.700(5)	23.662(4)	25.658(5)	16.566(3)
β, deg	90	90	102.919(2)	90
cell volume, Å^3	1992.7(7)	1993.0(5)	3909.8(13)	1780.1(5)
Z	4	4	8	4
D_c, g cm^{-3}	1.458	1.751	1.731	1.445
μ, mm^{-1}	0.634	5.545	5.753	0.699
F(000)	912	1040	2016	808
indep reflns	3911 [R_{int} = 0.0295]	4352 [R_{int} = 0.0674]	15348 [R_{int} = 0.0446]	3077 [R_{int} = 0.0367]
data/restraints/param	3911/2/236	4352/2/237	15348/196/793	3077/164/191
GOF on F^2	1.196	1.064	0.995	1.073
R1 [$I > 2\sigma(I)$]	0.0243	0.0297	0.0316	0.0607
wR$_2$ (all data)	0.0560	0.0734	0.0670	0.1642
largest diff peak/hole, e Å^{-3}	0.372/−0.455	2.115/−1.135	2.013/−0.892	1.803/−1.145
Flack parameter	0.03(3)	0.023(12)	−0.005(6)	a

[a] The calculated Flack parameter for **9** is meaningless [−1.05(17)] because only a few Friedel pairs have been measured.

Nb(OEt)$_4$(OC(O)CH(CH$_2$CH$_2$CH$_2$)NH-κO,κN) (**9**): colorless solid, 0.251 g and 90% yield from **1a** (0.200 mL, 0.800 mmol) and ProH (0.083 g, 0.721 mmol). Needlelike crystals suitable for X-ray analysis were collected from toluene/hexane at −30 °C. Anal. Calcd for $C_{13}H_{28}NNbO_6$: C, 40.32; H, 7.29; N, 3.62; Nb, 23.99. Found: C, 39.16; H, 7.15; N, 3.67; Nb, 23.20. IR (solid state): 3130m-br, 2971w-m, 2929w, 2861w-m, 1645vs, 1470w, 1443w, 1364m-s, 1318w, 1291w, 1262w, 1212w, 1142w, 1095s, 1051vs, 983w, 911vs, 850w, 798w, 778w, 699w-m cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.47, 4.14 (m, 8 H, OCH_2); 4.21 (m, 1 H, NCH); 3.69, 3.20, 2.22, 2.05, 1.84, 1.78 (m, 6 H, CH_2 *ring*); 3.30 (s-br, 1 H, NH); 1.22 (m-br, 12 H, OCH$_2$CH_3). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 178.2 (CO); 71.5, 68.8 (OCH$_2$CH$_3$); 65.0 (NCH); 49.7 (NCH$_2$); 30.6, 26.6 (CH$_2$ *ring*); 18.7, 18.2 (OCH$_2$CH$_3$). ^{93}Nb (CD$_2$Cl$_2$): δ −1185 ($\Delta\nu_{1/2}$ = 1.0 × 10^4 Hz).

Ta(OEt)$_4$(OC(O)CH(CH$_2$CH$_2$CH$_2$)NH-κO,κN) (**10**): colorless solid, 0.329 g and 91% yield from **1b** (0.22 mL, 0.851 mmol) and ProH (0.088 g, 0.760 mmol). Anal. Calcd for $C_{13}H_{28}NO_6Ta$: C, 32.85; H, 5.94; N, 2.95; Ta, 38.07. Found: C, 32.33; H, 6.07; N, 2.70; Ta, 38.11. IR (solid state): 3125m-br, 2972m, 2866m, 1639s, 1470w, 1443w, 1363m-s, 1320w-m, 1291w, 1144w-sh, 1101s, 1064s, 986w-m, 914s, 845m, 796w, 782w-m, 698m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.47, 4.17 (m, 8 H, OCH_2); 4.30 (m, 1 H, NCH); 3.71, 3.19, 2.27, 2.16, 1.93, 1.79 (m, 6 H, CH_2 *ring*); 3.25 (s, 1 H, NH); 1.28 (m-br, 12 H, OCH$_2$CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 178.1 (CO); 71.8, 67.1 (OCH$_2$CH$_3$); 64.8 (NCH); 49.7 (NCH$_2$); 30.6, 26.8 (CH$_2$ *ring*); 18.8, 18.5 (OCH$_2$CH$_3$).

2. Synthesis of Ta(OEt)$_4$[O$_2$CCH(NH$_2$)CH$_2$CH$_2$S(CH$_3$)(AuCl)] (11). A solution of Ta(OEt)$_4$(Met) and **10** (0.129 g, 0.253 mmol) in CH$_2$Cl$_2$ (10 mL) was added to Au(CO)Cl (0.066 g, 0.254 mmol). Progressive turning of the solution color to violet and gas release were noticed. The stirring was maintained for 18 h. The final solution was concentrated up to ca. 3 mL, layered with pentane, and stored at −30 °C for 3 days. Compound **11** was recovered as a violet microcrystalline solid. Yield: 0.160 g, 85%. Anal. Calcd for $C_{13}H_{30}AuClNO_6STa$: C, 21.05; H, 4.08; N, 1.89; Cl, 4.78. Found: C, 20.89; H, 4.02; N, 1.94; Cl, 4.64; IR (solid state): 3214m-br, 3145w, 2967m, 2869w, 1668s, 1582m-br, 1440m, 1379m-s, 1260s, 1097m, 1062m-s, 920vs, 864w, 794vs cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.68, 4.48 (m, 8 H, OCH_2); 3.74 (m, 1 H, NCH); 3.38, 2.53 (br, 2 H, NH_2); 2.77 (br, 2 H, SCH_2); 2.23, 2.11 (br, 2 H, SCH$_2$CH_2); 2.44 (s, 3 H, SCH_3); 1.34 (m, 12 H, OCH$_2$CH_3). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 177.4 (CO); 71.3, 67.6 (OCH$_2$CH$_3$); 58.4 (NCH); 32.8 (SCH$_2$CH$_2$); 29.8 (SCH$_2$); 18.2, 18.0 (OCH$_2$CH$_3$); 17.6 (SCH$_3$).

A gas-volumetric experiment showed that the reaction of **8** (0.305 g, 0.411 mmol) with 1 equiv of Au(CO)Cl, in *sym*-C$_2$H$_2$Cl$_4$, released CO (detected by gas chromatography) up to a CO/Au molar ratio = 0.99 after 6 h at 299 K.

3. X-ray Crystallographic Study. Crystal data and collection details for **2** and **7**−**9** are listed in Table 1. The diffraction experiment was carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction *SADABS*).[26] The structure was solved by direct methods and refined by full-matrix least squares based on all data using F^2.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions and refined by a riding model, except the N−H groups in **2** and **7**, which were located in the Fourier map and refined isotropically using the 1.2U_{iso} value of the parent nitrogen atom.

The asymmetric unit of the unit cell of **8** contains four independent molecules, showing very similar structures. Restraints were applied on the thermal parameters of **8** (SIMU 0.01 $C line in *SHEXL*) to help the refinement of light carbon atoms in the presence of tantalum atoms. In the case of **9**, restraints were applied to the thermal parameters of all atoms (SIMU 0.001) as well as on the O−C (DFIX 1.43 0.01) and C−C (DFIX 1.53 0.01) distances of the OEt groups in order to help the refinement because of the contemporary presence of heavy and lighter atoms. Details on all of the restraints applied have been included in the _refine_special_details section of the CIF files.

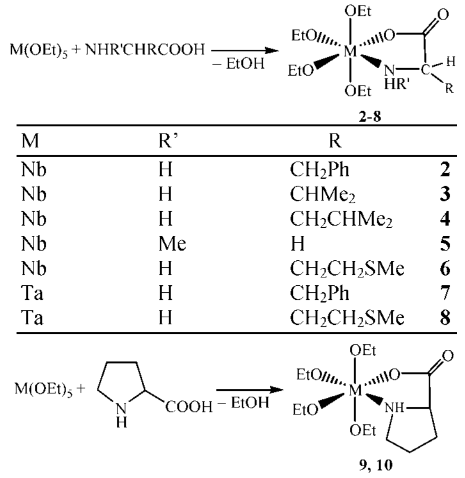
All four species (**2** and **7**−**9**) crystallize in chiral space groups ($P2_12_12_1$ for **2**, **7**, and **9**; P2$_1$ for **8**) and contain enantiopure complexes displaying the original L configuration of the amino acid at C(2). The crystals of **2** and **7** are isomorphous. The absolute structure of **9** is not completely reliable because only a few Friedel pairs have been measured.

4. Polymerization Reactions. In a typical procedure, a 25 mL flask, equipped with a magnetic stirring bar, was charged with the appropriate amounts of monomer and metal complex, respectively; see Table 4. The flask was then heated at 135 °C for 15 h. Afterward, the reaction was quenched by the addition of CH$_3$OH (ca. 5 mL). The polymer, obtained as a colorless precipitate, was dissolved in the minimum amount of CH$_2$Cl$_2$, and then CH$_3$OH was added to cause precipitation. The resulting solid was washed with CH_3OH (2 × 30 mL) and then dried in vacuo at 50 °C for 12 h.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of α-Aminoacidato Complexes of Niobium(V) and Tantalum(V). Niobium and tantalum pentaethoxides, **1a** and **1b**, reacted with a series of α-aminoacids in ca. 1:1 molar ratio in dichloromethane, according to Scheme 1. The reactions proceeded slowly because of the insolubility of the organic reactant in the reaction medium but afforded clean solutions after stirring overnight at room temperature. Compounds **2**−**10** were isolated as colorless crystalline compounds, stable in air for short periods of time, and readily soluble in toluene and halogenated hydrocarbons. According to NMR experiments, the formation of **2**−**10** is accompanied by the release of ethanol.

Scheme 1. Reaction of Niobium and Tantalum Pentaethoxides with α-Aminoacids



2-8

M	R'	R	
Nb	H	CH_2Ph	**2**
Nb	H	$CHMe_2$	**3**
Nb	H	CH_2CHMe_2	**4**
Nb	Me	H	**5**
Nb	H	CH_2CH_2SMe	**6**
Ta	H	CH_2Ph	**7**
Ta	H	CH_2CH_2SMe	**8**

9, 10

Compounds **2**−**10** were characterized by IR and NMR spectroscopy and elemental analysis. Moreover, the molecular structures of **2** and **7**−**9** were ascertained by X-ray diffraction (see Figures 1−3 and Table 2). Compounds **2** and **7** are isostructural, and their crystals are isomorphous; thus, they are both represented in Figure 1.

All of the complexes display a distorted octahedral geometry, with O,N-coordinated aminoacidate forming a stable five-membered chelate and occupying two cis positions,[28] whereas four ethoxide ligands are present in the other four sites. Compounds **2** and **7**−**9** represent the first examples of structurally characterized niobium and tantalum complexes containing a coordinated aminoacidato ligand.

The bonding parameters in the four complexes are very similar, with the M−OEt distances [1.8814(18)−1.922(5) Å] considerably shorter than the M−O(1) ones [2.097(5)−2.1156(18) Å] involving the aminoacidate. This is probably due to the fact that the negative charge in the latter is delocalized over the carboxylato group, whereas the charge is localized on the oxygen in the ethoxo ligands. This is confirmed by the fact that the C(1)−O(1) interaction [1.278(15)−1.298(3) Å] is only slightly shorter than that of C(1)−O(2) [1.208(16)−1.227(9) Å], and both interactions display some π character. C(1) shows almost the exact same sp^2 hybridization in all of the complexes [sum angles at C(1): 359.9(5), 359.8(9), 360.0(12), and 360.0(15)° for **2** and **7**−**9**, respectively], whereas C(2) is nearly tetrahedral [C(1)−C(2)−N(1): 108.5(3), 107.9(5), 109.9(6), and 108.5(9)°, respectively].

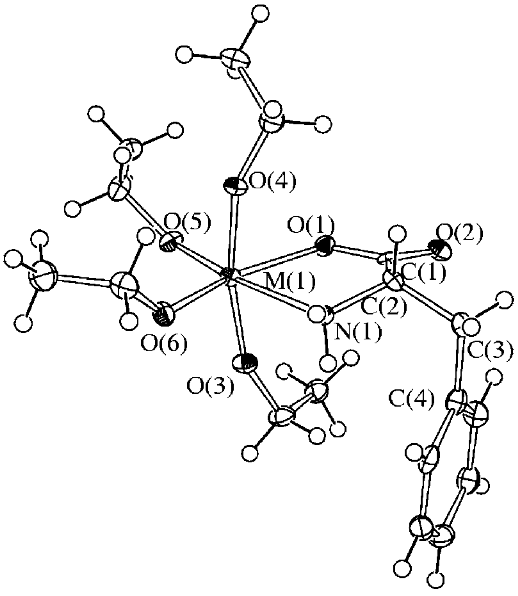


Figure 1. Molecular structure of **2** and **7** with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

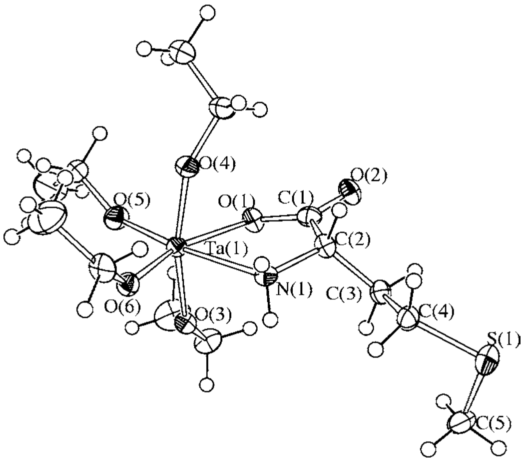


Figure 2. Molecular structure of **8** with key atoms labeled. Displacement ellipsoids are at the 50% probability level. Only one of the four independent molecules present in the unit cell is represented.

In all four crystals, the amino group of one molecule acts as a hydrogen-bond donor toward the O(2) atom of an adjacent molecule, thus generating an infinite 1D hydrogen-bonded chain in the cases of **2**, **7**, and **9**. Conversely, the hydrogen bonds in compound **8** involve also one ethoxide ligand per molecule, originating a more complex 2D network. An expanded view of the unit cell of compounds **2** and **8**, showing the molecules interconnected through hydrogen bonds, is reported in parts A and B of Figure 4, respectively. Figures SI1−SI3, given as Supporting Information, show a colored view of the 1D and 2D interconnections within compounds **2**, **8**, and **9**. Information about hydrogen bonds is summarized in Table 3.

The IR spectra of **2**−**10** show strong absorptions in the regions 1660−1630 and 1380−1350 cm^{-1}, assigned respectively to $\nu_{asym,COO}$ and $\nu_{sym,COO}$. In agreement with earlier

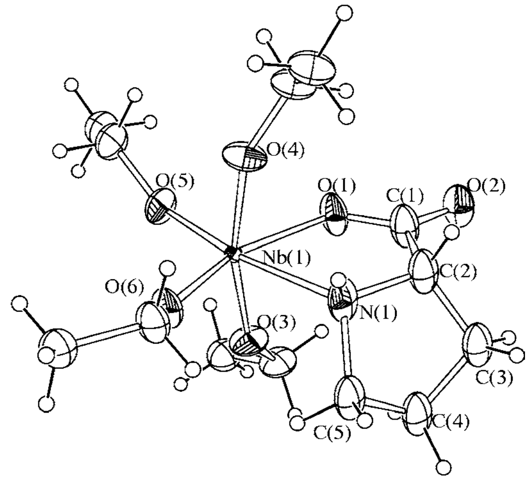


Figure 3. Molecular structure of **9** with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

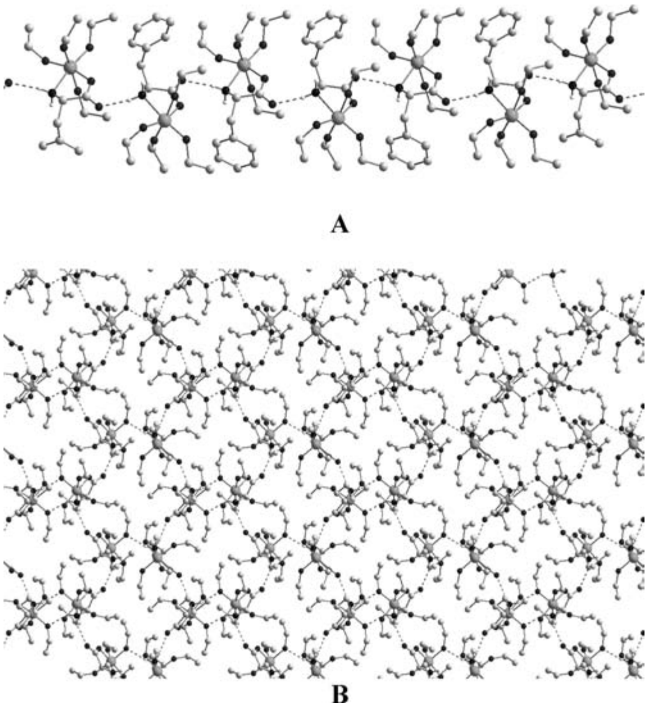


Figure 4. Expanded views of the unit cell of compounds **2** (A) and **8** (B), showing the molecules interconnected through hydrogen bonds.

reports on the coordination behavior of aminoacids toward metal centers,[29] the $\nu_{\mathrm{asym,COO}}$ vibrations are shifted to higher wavenumbers, whereas the $\nu_{\mathrm{sym,COO}}$ modes are shifted to lower frequencies, in comparison with the noncoordinated aminoacids. The increased difference between the wavenumbers of the two stretching vibrations has been considered to be diagnostic for the unidentate coordination of the carboxylato moiety of the aminoacidato ligand.[29]

The NMR data recorded for solutions of **2**−**10** in chlorinated solvents are in agreement with the X-ray features discussed above. Resonances assigned to nonequivalent ethoxy groups fall in the restricted ranges of chemical shifts [e.g., for **7** in $CDCl_3$: $\delta(^1H)$ 4.49, 4.39 (OCH_2), 1.23 (OCH_2CH_3); $\delta(^{13}C)$ 69.8, 66.5 (OCH_2), 19.2, 18.8 (OCH_2CH_3). for **4**: $\delta(^1H)$ 4.27, 4.05 (OCH_2), 1.04 (OCH_2CH_3); 0.80, 0.77 (m, 6 H, $CHCH_3$); $\delta(^{13}C)$ 71.5, 68.7, 67.7, 67.0 (OCH_2CH_3), 18.6, 18.2, 17.5 (OCH_2CH_3)]. The protons belonging to the $-NH_2$ group (compounds **2**, **3**, and **6**−**8**) give two distinct resonances due to inhibition of the C−N rotation within the five-membered metallacycle. Two possible orientations of the different N-substituents are predictable for the sarcosinato complex **5** (the nitrogen atom becomes asymmetric upon coordination); indeed, two isomeric forms have been detected in solution, with one largely prevalent (see the Experimental Section).

The salient ^{13}C feature in **2**−**10** is represented by the carbonyl resonance, which falls within the range δ 174.9 (**5**)−

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2 and 7−9

	2	7	8	9
M(1)−O(1)	2.1156(18)	2.100(3)	2.097(5)	2.109(8)
M(1)−N(1)	2.321(2)	2.307(4)	2.294(5)	2.301(10)
M(1)−O(3)	1.8814(18)	1.896(3)	1.922(5)	1.885(7)
M(1)−O(4)	1.8993(18)	1.911(3)	1.885(5)	1.903(7)
M(1)−O(5)	1.9015(17)	1.897(4)	1.883(5)	1.901(7)
M(1)−O(6)	1.8938(18)	1.895(3)	1.888(5)	1.887(7)
C(1)−O(1)	1.298(3)	1.294(6)	1.294(9)	1.278(15)
C(1)−O(2)	1.222(3)	1.222(6)	1.227(9)	1.208(16)
C(1)−C(2)	1.542(3)	1.542(6)	1.536(9)	1.568(17)
C(2)−N(1)	1.473(4)	1.469(7)	1.487(8)	1.502(16)
C(2)−C(3)	1.526(4)	1.524(7)	1.522(9)	1.519(11)
O(1)−M(1)−O(6)	159.27(7)	160.19(14)	159.0(2)	159.1(4)
N(1)−M(1)−O(5)	170.08(8)	169.50(14)	170.6(2)	170.8(4)
O(3)−M(1)−O(4)	167.99(8)	168.54(15)	167.2(2)	166.1(5)
O(1)−M(1)−N(1)	72.50(7)	72.64(14)	73.35(18)	74.7(4)
M(1)−O(1)−C(1)	124.90(18)	124.8(3)	124.3(4)	123.4(7)
O(1)−C(1)−O(2)	123.7(3)	124.2(5)	124.2(7)	123.3(11)
O(1)−C(1)−C(2)	114.9(3)	114.8(5)	116.4(6)	118.9(10)
O(2)−C(1)−C(2)	121.3(3)	120.8(5)	119.4(7)	117.8(11)
C(1)−C(2)−N(1)	108.5(3)	107.9(5)	109.9(6)	108.5(9)
C(2)−N(1)−M(1)	113.12(16)	113.4(3)	113.5(4)	114.2(7)

Table 3. N(1)−H−O(2)#1 Hydrogen Bonds (Å and deg) for 2 and 7−9

	2	7	8[a]	9
N(1)−H	0.885(10)	0.885(19)	0.92	0.93
H···O(2)	2.035(12)	2.03(2)	2.02	2.05
N(1)···O(2)	2.906(3)	2.906(5)	2.909(7)	2.931(16)
N(1)−H−O(2)	168(3)	171(5)	162.1	158.1
symmetry transformation #1	$-x, y - {}^1/_2, -z + {}^1/_2$	$-x + 1, y + {}^1/_2, -z + {}^1/_2$	$x, y - 1, z$	$x - {}^1/_2, -y + {}^1/_2, -z + 2$

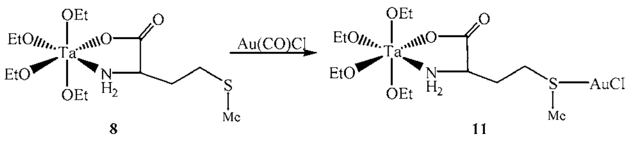
[a] A second hydrogen bond between N(1) (donor) and one ethoxide (acceptor), O(24), is present: N(1)−H, 0.92 Å; H···O(24), 2.22 Å; N(1)···O(24), 3.010(7) Å; N(1)−H−O(24), 143.3°.

178.3 (**4**). Furthermore, the ^{93}Nb NMR spectra of **2**−**6** and **9** display a very broad resonance around δ −1200.

The alkoxide complexes **1a** and **1b** did not undergo substitution of more than 1 equiv of aminoacid reactant. In particular, the reaction of **1a** was tried with a 4-fold molar excess of PheH at high temperature, leading to the isolation of **2** in very good yield (see the Experimental Section).

Current interest in early−late heterobimetallic (ELHB) complexes stems from the expectation for their cooperative reactivities originating from the combination of electropositive early metals and electron-rich late metals.[30] Considering that heterobimetallics containing bridging sulfur atoms have attracted significant attention because of their possible relevance to biological systems and industrial processes,[31] we viewed compound **8** as a potential sulfur ligand for a soft metal center. Thus, **8** was allowed to react with a stoichiometric amount of Au(CO)Cl in CH_2Cl_2 at room temperature; the reaction took place with CO release[32] (up to CO/Au molar ratio = 0.99 in *sym*-$C_2H_2Cl_4$), affording the air-sensitive derivative **11** (Scheme 2).

Scheme 2. Preparation of the Tantalum/Gold Bimetallic Derivative 11



Although we were not able to grow X-ray quality crystals of **11**, its structure was deduced from spectroscopic data and confirmed by analytical data. More precisely, the IR spectrum of **11** shows strong absorptions at 1668 and 1379 cm^{-1} (compared to 1661 and 1377 cm^{-1} observed in **8**), assigned to the $\nu_{asym,COO}$ and $\nu_{sym,COO}$ stretching vibrations, respectively. This feature suggests that the aminoacidato frame undergoes negligible change upon passing from **8** to **11**.

The ^{1}H NMR spectrum of **11** (in CD_2Cl_2) shows the expected pattern for the coordination of **8** to gold through the sulfur atom; in particular, the resonance related to the −SMe group shifts from δ 2.12 to 2.44.[33] The ^{13}C NMR spectrum of **11** displays a unique resonance in the carbonyl region (δ 177.4), attributed to the aminoacidato moiety, thus confirming the loss of carbon monoxide from the gold center.

Although ELHB species containing niobium or tantalum are a well-known class of compounds,[2a,34] **11** represents a rare example of a tantalum−gold heterobimetallic derivative.[35]

Ring-Opening Polymerization (ROP) of L- and D,L-LA. Polylactide (PLA), together with polyglycolide and polycaprolactone, belongs to a class of commercially available biodegradable polyesters, which have attracted hugely increasing attention for their numerous environmental advantages.[36] Among the wide-ranging applications, medical uses of the polymers deserve to be cited, including sutures, bone fillers, tissue engineering, and controlled drug delivery.[37]

Recently, we reported on the ROP of D,L-LA initiated by *N*,*N*-dialkylcarbamates of group 4 elements.[38] The investigation on the behavior of the new alkoxo aminoacidates in LA polymerization appeared intriguing for two points. First, the presence of a chiral center in the complexes **2**−**5**, **7**, **9**, and **10** may induce, in principle, some stereocontrol during the polymerization process; the extent of stereocontrol is an important issue because the physical and degradation properties of the PLA depend upon the tacticity of the polymer.[39] Furthermore, to the best of our knowledge, only one case has been reported on the successful use of tantalum compounds in the ROP of LAs.[3e] In fact, a number of attempts to employ tantalum species as possible initiators of LA polymerization revealed the absence of activity: the list of tested, nonreactive compounds include $Ta(OR)_2$[tris(2-oxy-3,5-dimethylbenzyl)-amine] (R = Me or Et)[3e] and $Ta(O_2CNR_2)_5$ (R = Me, Et).[40]

The ROP of D,L- and L-LA initiated by complexes **1a**, **1b**, **2**, and **7** was carried out in bulk at 135 °C with [LA]/[M] ratio = 300; the polymerization results are presented in Table 4. Interestingly, the tantalum compounds **1b** and **7** worked as polymerization promoters.[3e] Nevertheless, the niobium complexes afforded higher conversions than the tantalum analogues (see Table 4). Moreover, the aminoacidato complexes **2** and **7** were more active than the parent compounds **1a** and **1b**.

Table 4. Results of L- and D,L-LA Bulk Polymerizations[a]

catalyst (g)	LA	polymer (g)	yield (%)	T_g[b] (°C)	T_m[c] (°C)	M_w[d] (Da)	M_w/M_n[d]	P_r[e]
1a (0.040)	L-LA	1.57	91	50.8	166.3	26100	1.6	
1a (0.040)	D,L-LA	1.37	80	46.2		25900	1.6	0.42
2 (0.039)	L-LA	1.88	95	55.9	166.1	23000	1.5	
2 (0.033)	D,L-LA	1.24	86	45.2		21000	1.7	0.54
1b (0.040)	L-LA	1.47	85	56.4	164.3	22000	1.8	
1b (0.040)	D,L-LA	1.32	76	43.4		18700	1.8	0.40
7 (0.028)	L-LA	1.08	88	58.2	165.0	19000	1.7	
7 (0.026)	D,L-LA	0.85	77	43.2		17000	1.9	0.63

[a] Polymerization conditions: [LA]/[M] = 300 mol/mol (M = Nb or Ta); *t* = 15 h; oil bath temperature = 135 ± 5 °C; no solvent used. [b] Glass transition temperature T_g. [c] Melting temperature. [d] Measured by SEC analysis. [e] Probability of racemic linkage calculated from homonuclear-decoupled ^{1}H NMR analysis.

The ^{1}H NMR spectra of the obtained PLA samples show the presence of ethyl ester and hydroxy end groups; this evidence is in accordance with a coordination−insertion mechanism[36a,b,i,41] and suggests that the initiation occurs via insertion of the alkoxo moiety of the metal complex into the LA molecule. The homonuclear-decoupled ^{1}H NMR spectra of poly(L-LA) and poly(D,L-LA) materials allowed one to determine the microstructure of the polymers. Thus, L-LA polymerization reactions by complexes **1a**, **1b**, **2**, and **7** resulted in the formation of highly isotactic polymers. Otherwise, the polymerizations of D,L-LA initiated by complexes **1a** and **1b** formed fully atactic PLA with $P_r \approx 0.4$,[3e,42] whereas **2** and **7** gave a slightly heterotactic enchainment in the same conditions ($P_r = 0.54$ and 0.63, respectively; Table 4).

Gel permeation chromatography analysis of polymers gave M_n values ranging from 17000 to 26100 Da (Table 4). The polydispersity index values ($M_w/M_n = 1.5−1.9$) are indicative of relatively broad molecular weight distributions, somewhat higher than those expected for controlled polymerization. This phenomenon may be attributed to side transesterification reactions occurring in the course of the polymerization process.[42d,43]

According to differential scanning calorimetry measurements, the isotactically pure PLAs obtained from L-LA and **1a**, **1b**, **2**, and **7** are crystalline materials exhibiting glass transition temperatures T_g = 50−58 °C and melting temperatures T_m = 164−166 °C. On the other hand, the polymers provided by the same initiators from the ROP of D,L-LA exhibited lower T_g (43−46 °C) and no melting temperature.

■ CONCLUSIONS

The straightforward synthesis of natural α-aminoacidato derivatives of niobium(V) and tantalum(V) ethoxides has been reported, including the first examples of crystallographically characterized coordination adducts of such metals bearing an aminoacidato ligand. The products form from the parent homoleptic ethoxides by interaction with the amino acid reactant via rupture of the dinuclear structure and loss of one ethanol molecule per metal. The reactivity of the new complexes has been investigated in two different contexts. Thus, the association of Au(CO)Cl with the tantalum methionato species has afforded a rare example of a tantalum−gold heterobimetallic complex, proving that the methionato ligand may act as an effective sulfur donor. Moreover, a selection of niobium/tantalum products have been tested as catalytic precursors for the ROP of L-LA and D,L-LA. Although the niobium species were revealed to be more active than the corresponding tantalum ones, the unusual capability of the latter to promote the polymerization reaction has been detected. The presence of the chiral ligand supplies some asymmetric character to the catalytic centers, in comparison with the parent alkoxide complexes; possible developments in the use of the novel aminoacidato complexes in asymmetric homogeneous catalysis will be the subject of future reports.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Expanded view of the unit cell of compounds **2**, **8**, and **9**, detailing the molecules interconnected through hydrogen bonds (Figures SI1−SI3). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference numbers 918361 (**2**), 918363 (**7**), 918364 (**8**), and 918362 (**9**) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (international) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk].

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Notes

The authors declare no competing financial interest.

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