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

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TITLE RUNNING HEAD: α-Aminoacidato Ethoxides of Nb(V) and Ta(V)

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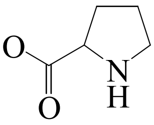
Abstract

High yields of the ethoxo-α-aminoacidates of 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 $M(OEt)_4$( -κO,κN) (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 dichloromethane solution. The new complexes **2-10** have been fully characterized by spectroscopic and analytical methods, and by X-ray diffraction for **2**, **7, 8** and **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 the 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 PLA with $P_r \approx 0.4$.

Introduction

The chemistry of metal alkoxides, which dates back to more than 100 years, has received growing attention by a number of research groups during the last 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 (CVD),[2] catalysis,[3] and as precursors of M_2O_5 nanospheres,[4] nanorods,[5] microporous membranes,[6] electro-optic 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.[8,9,10]

Our recent interest in the chemistry of oxygen donor species with niobium and tantalum derivatives,[11] consisting in the preparation and the 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 proved 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] 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 Nb(V) aqueous system was reported,[18] however the only example of well-defined coordination compound is, to the best of our knowledge, a cyclopentadienyl-alaninato 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 alloys surfaces by the addition of short amino acid sequences has proved 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 bridged methionato ligand. Furthermore, the lactide 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 atmosphere of pre-purified 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 argon atmosphere as received. L-phenylalanine (PheH), L-valine (ValH), L-leucine (LeuH), L-proline

(ProH) (Apollo Scientific), sarcosine (SarH), L-methionine (MetH), L-lactide and D,L-lactide (Sigma-Aldrich) were commercial products of the highest purity available, stored under 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 appropriate drying agents under argon atmosphere before use: CH_2Cl_2, CD_2Cl_2 and $CDCl_3$ from P_4O_{10}, toluene from Na, hexane and heptane from $LiAlH_4$. Infrared spectra were recorded at 298 K on FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. NMR spectra were recorded at 298 K on Bruker Avance DRX400 instrument equipped with BBFO broadband probe. The chemical shifts for ^1H and ^{13}C were referenced to the non-deuterated 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 Carlo Erba mod. 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 down to room temperature and 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), by using chloroform as eluent (1 mL/min), a HPLC 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 the calibration of the columns.

1) General synthesis of $M(OEt)_4$(aminoacidato) complexes. The synthesis of $Nb(OEt)_4[OC(O)CH(CH_2Ph)NH_2-\kappa O,\kappa N]$, **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 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 standard. NMR analyses performed at the end of the reactions showed the presence of EtOH (EtOH/$CHCl_3$ ratio = 1) in all cases.

$Nb(OEt)_4[OC(O)CH(CH_2Ph)NH_2–\kappa O,\kappa N]$, 2. A suspension of L-phenylalanine (0.119 g, 0.720 mmol) in CH_2Cl_2 (15 mL), was treated with $Nb(OEt)_5$, **1a** (0.200 mL, 0.797 mmol). The resulting mixture was stirred at room temperature for 18 hours, 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 hours. Yield: 0.266 g, 85%. The reaction of L-phenylalanine (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 hours: 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, NC*H*); 3.28 (m, 2 H, CH_2Ph); 2.97, 2.55 (m, 2 H, NH_2); 1.23 ppm (m-br, 12 H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 176.0 (*C*O); 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 ppm (OCH_2CH_3). ^{93}Nb NMR ($CDCl_3$): δ = −1201 ppm ($\Delta\nu_{1/2} = 1.1\cdot10^4$ Hz).

$Nb(OEt)_4[OC(O)CH(CHMe_2)NH_2–\kappa O,\kappa N]$, 3. Colorless solid, 0.291 g, 86% yield from **1a** (0.250 mL, 1.00 mmol) and L-valine (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, NC*H*); 3.56, 2.57 (br, 2 H, NH_2); 2.68 (m, 1 H, $CHCH_3$); 1.28 (m-br, 12 H, OCH$_2$C*H*$_3$); 1.06, 0.94 ppm (m, 6 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 176.3 (*C*O); 68.7, 67.9, 67.3 (O*C*H$_2$CH$_3$); 63.3 (N*C*H); 30.1 (*C*HCH$_3$); 19.3, 15.8 (CH*C*H$_3$); 18.7, 18.2 ppm (OCH$_2$*C*H$_3$). ^{93}Nb NMR (CDCl$_3$): δ = −1180 ppm (Δν½ = 2.0·10^4 Hz).

Nb(OEt)$_4$[OC(O)CH(CH$_2$CHMe$_2$)NH$_2$–κO,κN], 4. Colorless solid, 0.319 g, 88% yield from **1a** (0.25 mL, 1.00 mmol) and L-leucine (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}. ^{1}H NMR (CDCl$_3$): δ = 4.27 (q, ^{3}J$_{HH}$ = 6.97 Hz, 6 H, OC*H*$_2$); 4.05 (q, ^{3}J$_{HH}$ = 6.60 Hz, 2 H, OC*H*$_2$); 3.46 (m, 1 H, C*H*NH$_2$); 3.04 (br, 1 H, N*H*), 2.38 (m, 1 H, N*H*); 1.81, 1.35 (m, 2 H, CHC*H*$_2$), 1.64 (s, 1 H, C*H*CH$_3$); 1.04 (m, 12 H, OCH$_2$C*H*$_3$); 0.80, 0.77 ppm (m, 6 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 178.3 (*C*O); 71.5, 68.7, 67.0 (O*C*H$_2$CH$_3$); 56.0 (*C*HNH$_2$); 43.3 (CH*C*H$_2$); 24.7 (*C*HCH$_3$); 23.2, 20.8 (CH*C*H$_3$); 18.6, 18.2, 17.5 ppm (OCH$_2$*C*H$_3$). ^{93}Nb (CDCl$_3$): δ = −1154 ppm (Δν½ = 2.0·10^4 Hz).

Nb(OEt)$_4$[OC(O)CH$_2$NHMe–κO,κN], 5. Colorless solid, 0.191 g, 74% yield from **1a** (0.200 mL, 0.797 mmol) and sarcosine (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}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 4.47, 4.24 (m, 8 H, OC*H*$_2$); 3.85 (br, 2 H, NC*H*$_2$); 3.14 (br, 1 H, N*H*); 2.59, *2.48* (s, 3 H, NC*H*$_3$); 1.24 ppm (m, 12 H, OCH$_2$C*H*$_3$). Isomer ratio 8:1. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 174.9 (*C*O); 68.8, 67.9 (O*C*H$_2$CH$_3$); 57.4, *54.6* (N*C*H$_2$); 38.8, *36.1* (N*C*H$_3$); 18.7, 18.3, 17.6 ppm (OCH$_2$*C*H$_3$). ^{93}Nb (CD$_2$Cl$_2$): δ = −1195 ppm (Δν½ = 1.0·10^4 Hz).

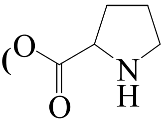
Nb(OEt)$_4$[OC(O)CH(CH$_2$CH$_2$SMe)NH$_2$–κO,κN], 6. Colorless solid, 0.255 g, 84% yield from **1a** (0.200 mL, 0.797 mmol) and L-methionine (0.107 g, 0.721 mmol). Anal. Calcd for $C_{13}H_{30}NNbO_6S$: C, 37.06; H, 7.18; N, 3.32; Nb, 22.05. Found: C, 36.80; H, 7.11; N, 3.60; Nb, 22.21. IR (solid state):

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}. ^{1}H NMR (CD_2Cl_2): δ = 4.45, 4.21 (m, 8 H, OCH_2); 3.80 (m, 1 H, NC*H*); 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 ppm (m, 12 H, OCH_2CH_3). Isomer ratio *ca.* 1.1: 1. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 177.2 (*C*O); 71.3, 68.7, 67.8, 67.2 (OCH_2CH_3); 57.1 (N*C*H); 32.3 (SCH_2CH_2); 30.6 (SCH_2); 18.6, 18.2, 17.5 (OCH_2CH_3); 14.8 ppm (SCH_3). ^{93}Nb (CD_2Cl_2): δ = −1194 ppm (Δν½ = 1.3·10^4 Hz).

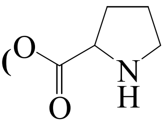
Ta(OEt)$_4$[OC(O)CH(CH$_2$Ph)NH$_2$–κO,κN], 7. Colorless solid, 0.302 g, 79% yield from **1b** (0.210 mL, 0.810 mmol) and L- phenylalanine (0.120 g, 0.730 mmol). Crystals suitable for X ray analysis were collected from CH_2Cl_2/hexane at −30°C. Anal. Calcd for $C_{17}H_{30}NO_6Ta$: C, 38.86; H, 5.76; 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}. ^{1}H 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, NC*H*); 3.29 (m, 2 H, CH_2Ph); 3.15, 2.68 (m, 2 H, NH_2); 1.23 ppm (m-br, 12 H, OCH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 176.5 (*C*O); 136.0 (*ipso*-Ph); 129.7, 129.3, 127.7 (C_6H_5); 69.8, 66.5 (OCH_2CH_3); 58.5 (N*C*H); 39.1 (CH_2Ph); 19.2, 18.8 ppm (OCH_2CH_3).

Ta(OEt)$_4$[OC(O)CH(CH$_2$CH$_2$SMe)NH$_2$–κO,κN], 8. Colorless solid, 0.331 g, 80% yield from **1b** (0.23 mL, 0.900 mmol) and L-methionine (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}. ^{1}H NMR (CD_2Cl_2): δ = 4.62, 4.33 (m, 8 H, OCH_2); 3.91 (m, 1 H, NC*H*); 3.25, 2.40 (br, 2 H, NH_2); 2.66 (m, 2 H, SCH_2); 2.55, 2.03 (m, 2

H, SCH$_2$C*H*$_2$); 2.12 (s, 3 H, SC*H*$_3$); 1.32 ppm (m, 12 H, OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ= 175.9 (*C*O); 71.6, 69.2 (O*C*H$_2$CH$_3$); 57.1 (N*C*H); 32.6 (SCH$_2$*C*H$_2$); 30.9 (S*C*H$_2$); 18.1 (OCH$_2$*C*H$_3$); 14.8 ppm (S*C*H$_3$).

Nb(OEt)$_4$(


-κO,κN), 9. Colorless solid, 0.251 g, 90% yield from **1a** (0.200 mL, 0.800 mmol) and L- proline (0.083 g, 0.721 mmol). Needle-like 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, OC*H*$_2$); 4.21 (m, 1 H, NC*H*); 3.69, 3.20, 2.22, 2.05, 1.84, 1.78 (m, 6 H, C*H*$_2$ *ring*); 3.30 (s-br, 1 H, N*H*); 1.22 ppm (m-br, 12 H, OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 178.2 (*C*O); 71.5, 68.8 (O*C*H$_2$CH$_3$); 65.0 (N*C*H); 49.7 (N*C*H$_2$); 30.6, 26.6 (*C*H$_2$ *ring*); 18.7, 18.2 ppm (OCH$_2$*C*H$_3$). ^{93}Nb (CD$_2$Cl$_2$): δ= −1185 ppm ($\Delta\nu_{½}$ = $1.0\cdot10^4$ Hz).

Ta(OEt)$_4$(


-κO,κN), 10. Colorless solid, 0.329 g, 91% yield from **1b** (0.22 mL, 0.851 mmol) and L-proline (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-broad, 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, OC*H*$_2$); 4.30 (m, 1 H, NC*H*); 3.71, 3.19, 2.27, 2.16, 1.93, 1.79 (m, 6 H, C*H*$_2$ *ring*); 3.25 (s, 1 H, N*H*); 1.28 ppm (m-br, 12 H, OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ= 178.1 (*C*O); 71.8, 67.1 (O*C*H$_2$CH$_3$); 64.8 (N*C*H); 49.7 (N*C*H$_2$); 30.6, 26.8 (*C*H$_2$ *ring*); 18.8, 18.5 ppm (OCH$_2$*C*H$_3$).

2) Synthesis of $Ta(OEt)_4[O_2CCH(NH_2)CH_2CH_2S(CH_3)(AuCl)]$, 11. A solution of $Ta(OEt)_4(Met)$, **10** (0.129 g, 0.253 mmol), in CH_2Cl_2 (10 mL) was added of 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 hours. The final solution was concentrated up to *ca.* 3 mL, layered with pentane and stored at −30°C for 3 d. Compound **11** was recovered as 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}. ^1H NMR (CD_2Cl_2): $\delta = 4.68, 4.48$ (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_2CH_2); 2.44 (s, 3 H, SCH_3); 1.34 ppm (m, 12 H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 177.4$ (CO); 71.3, 67.6 (OCH_2CH_3); 58.4 (NCH); 32.8 (SCH_2CH_2); 29.8 (SCH_2); 18.2, 18.0 (OCH_2CH_3); 17.6 ppm (SCH_3).

A gas-volumetric experiment showed that the reaction of **8** (0.305 g, 0.411 mmol) with one equivalent of Au(CO)Cl, in *sym*-$C_2H_2Cl_4$, 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**, **7**, **8** and **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 N-H groups in **2** and **7** which were located in the Fourier map and refined isotropically using the 1.2 fold U_{iso} value of the parent N-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 .01 $C line in SHEXL) to help the refinement of light C atoms in the presence of Ta-atoms. In the case of **9**, restraints were applied to the thermal parameters of all atoms (SIMU .001) as well as on the O–C (DFIX 1.43 .01) and C–C (DFIX 1.53 .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 the restraints applied have been included in the _refine_special_details section of the cif files.

All the four species (**2**, **7**, **8**, **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 since only few Friedel pairs have been measured.

Table 1. Crystal data and experimental details for **2**, **7**, **8** and **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)
Crystal system	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, °	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
Independent reflections	3911 [R_{int} = 0.0295]	4352 [R_{int} = 0.0674]	15348 [R_{int} = 0.0446]	3077 [R_{int} = 0.0367]
Data / restraints / parameters	3911 / 2 / 236	4352 / 2 / 237	15348 / 196/ 793	3077 / 164 / 191
Goodness on fit on F^2	1.196	1.064	0.995	1.073
R_1 ($I > 2\sigma(I)$)	0.0243	0.0297	0.0316	0.0607
wR_2 (all data)	0.0560	0.0734	0.0670	0.1642
Largest diff. peak and 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)	*

* The calculated Flack parameter for **9** is meaningless [-1.05(17)] since only 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. Afterwards the reaction was quenched by the addition of

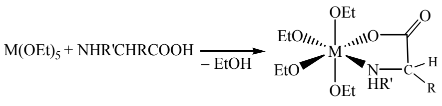
CH_3OH (*ca.* 5 mL). The polymer, obtained as a colorless precipitate, was dissolved in the minimum amount of CH_2Cl_2 and then CH_3OH was added to cause precipitation. The resulting solid was washed with CH_3OH (2 × 30 mL) and then dried in vacuo at 50 °C for 12 h.

Results and discussion

Synthesis and characterization of α-aminoacidato complexes of Nb(V) and Ta(V).

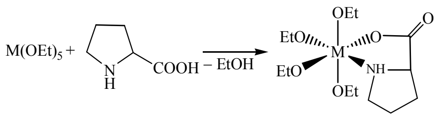
Niobium and tantalum pentaethoxides, **1a**,**b**, reacted with a series of α-amino acids in *ca.* 1:1 molar ratio in dichloromethane, according to Scheme 1. The reactions proceeded slowly due to the insolubility of the organic reactant in the reaction medium, but afforded clean solutions after stirring 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 release of ethanol.

Scheme 1. Reaction of niobium and tantalum pentaethoxides with α-amino acids.



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**, **7**, **8** and **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**, **7**, **8** and **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 C(1)–O(2) [1.208(16)-1.227(9) Å], and both interactions display some π-character. C(1) shows an almost exact *sp*^{2} hybridization in all the complexes [sum angles at C(1): 359.9(5), 359.8(9), 360.0(12) and 360.0(15)° for **2**, **7**, **8** and **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].

In all of the four crystals, the amino group of one molecule acts as a H-bond donor towards the O(2) atom of an adjacent molecule, thus generating an infinite 1D H-bonded chain in the cases of **2**, **7** and **9**. Conversely, the H-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 interconnected molecules through H-bonds, is reported in Figures 4A and 4B, respectively. Figures SI1-SI3, given as Supporting Information, show a colored view of the 1D- and 2D interconnections within compounds **2**, **8** and **9**. Informations about H-bonds are summarized in Table 3.

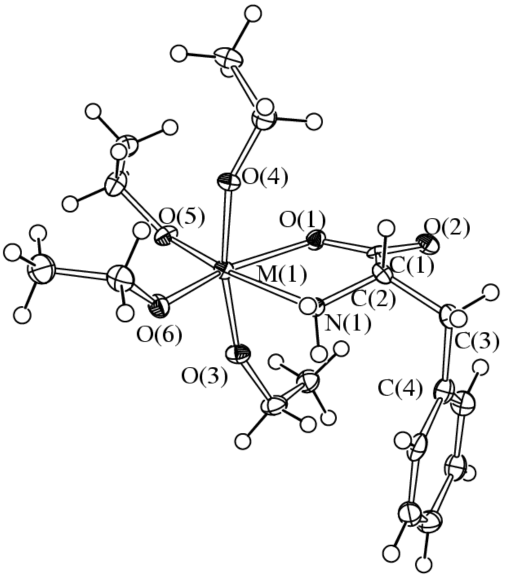


Figure 1. Molecular structure of $M(OEt)_4[OC(O)CH(CH_2Ph)NH_2$-κO,κN] (M = Nb, **2**; Ta, **7)** with key atoms labelled. Displacement ellipsoids are at the 50% probability level

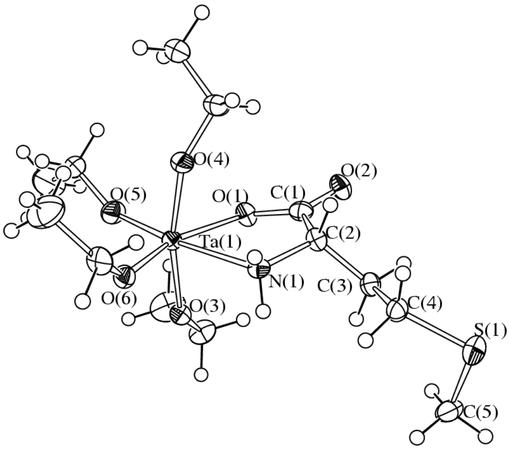


Figure 2. Molecular structure of $Ta(OEt)_4[OC(O)CH(CH_2CH_2SMe)NH_2$-κO,κN], **8** with key atoms labelled. Displacement ellipsoids are at the 50% probability level. Only one of the four independent molecules present in the unit cell is represented.

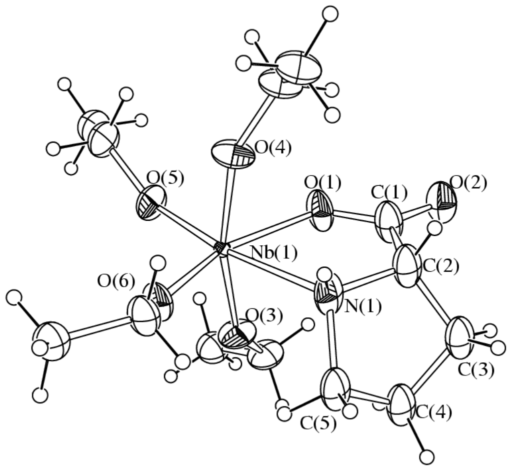


Figure 3. Molecular structure of **9** with key atoms labelled. Displacement ellipsoids are at the 50% probability level.

Table 2. Selected bond distances (Å) and angles (°) for **2**, **7**, **8** and **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)

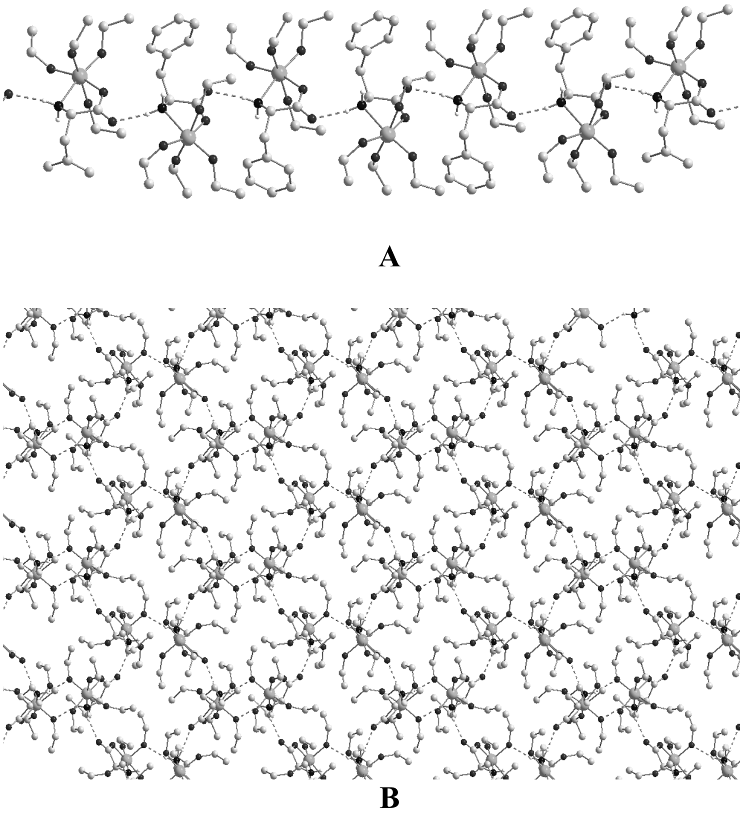


Figure 4. Expanded view of the unit cell of compounds **2 (A)** and **8 (B)**, showing the interconnected molecules through H-bonds.

Table 3. N(1)–H–O(2) #1 hydrogen bonds (Å and °) for **2**, **7**, **8** and **9**.

	2	**7**	**8**	**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 H-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°.

The infrared spectra of **2-10** show strong absorptions in the regions 1660-1630 cm^{-1} and 1380-1350 cm^{-1}, assigned respectively to the $\nu_{asym,COO}$ and $\nu_{sym,COO}$. In agreement with earlier reports on the coordination behavior of amino acids toward metal centres,[29] the $\nu_{asym,COO}$ vibrations are shifted to higher wavenumbers whereas the $\nu_{sym,COO}$ modes are shifted to lower frequencies, in comparison with the non coordinated amino acids. The increased difference between the wavenumbers of the two stretching vibrations has been considered diagnostic for the unidentate coordination of the carboxylato moiety of the aminoacidato ligand.[29]

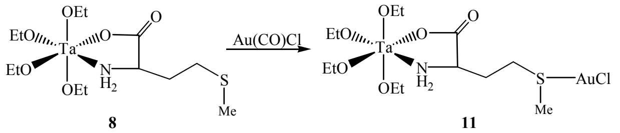
The NMR data recorded for solutions of **2-10** in chlorinated solvents are in agreement with the X-ray features discussed above. Resonances assigned to non equivalent ethoxy groups fall in restricted ranges of chemical shifts [*e.g.* for **7** in $CDCl_3$: $\delta(^1H)$ = 4.49, 4.39 (OCH_2), 1.23 ppm (OCH_2CH_3); $\delta(^{13}C)$ = 69.8, 66.5 (OCH_2), 19.2, 18.8 ppm (OCH_2CH_3). for **4**: $\delta(^1H)$ = 4.27, 4.05 (OCH_2), 1.04 ppm (OCH_2CH_3); 0.80, 0.77 ppm (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 ppm (OCH_2CH_3)]. The protons belonging to the $-NH_2$ group (compounds **2**, **3**, **6-8**) give two distinct resonances due to the 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 on coordination); indeed two isomeric forms have been detected in solution, with one largely prevalent (see Experimental).

Salient ^{13}C feature in **2-10** is represented by the carbonyl resonance, which falls in within the range 174.9 (**5**) - 178.3 ppm (**4**). Furthermore the ^{93}Nb spectra of **2-6** and **9** display a very broad resonance around −1200 ppm.

The alkoxide complexes **1a,b** did not undergo substitution of more than one equivalent of amino acid reactant. In particular, the reaction of **1a** was tried with a four-fold molar excess of L-phenylalanine at high temperature, leading to the isolation of **2** in very good yield (see Experimental).

Current interest in early-late heterobimetallic (ELHB) complexes stems from the expectation for their cooperative reactivities originated from the combination of electropositive early metals and electron-rich late metals.[30] On considering that heterobimetallics containing bridging sulphur atoms have attracted significant attention because of their possible relevance to biological systems and industrial processes,[31] we viewed compound **8** as a potential S-ligand for a soft metal centre. 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 $Ta(OEt)_4O_2CCH(NH_2)CH_2CH_2S(CH_3)(AuCl)]$, **11**, Scheme 2.

Scheme 2. Preparation of the Ta/Au 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 infrared spectrum of **11** shows strong absorptions at 1668 and 1379 cm^{-1} (to be 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 on 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 2.12 to 2.44 ppm.[33] The ^{13}C-NMR spectrum of **11** displays a unique resonance in the carbonyl region (δ = 177.4 ppm), attributed to the aminoacidato moiety, thus confirming the loss of carbon monoxide from the gold centre.

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

Ring-Opening Polymerization of L- and D,L-lactide

Polylactide, together with polyglycolide and polycaprolactone, belongs to the 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 ring-opening polymerization of D,L-lactide initiated by N,N-dialkylcarbamates of Group 4 elements.[38] The investigation on the behavior of the new alkoxo aminoacidates in lactide polymerization appeared intriguing for two points. First, the presence of a chiral centre in the complexes **2-5, 7, 9, 10** may induce, in principle, some stereocontrol during the polymerization process; the extent of stereocontrol is an important issue because the physical and the degradation properties of the polylactide 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 lactides.[3e] In fact, a number of attempts to employ tantalum species as possible initiators of lactide polymerization revealed absence of activity: the list of tested, non reactive 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]

Ring-opening polymerization of D,L- and L-lactide initiated by complexes **1a, 1b**, **2** and **7** were 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** resulted more active than the parent compounds **1a** and **1b**.

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 lactide molecule. The homonuclear decoupled ^{1}H-NMR spectra of poly(L-LA) and poly(D,L-LA) materials allowed to determine the microstructure of the polymers. Thus L-LA polymerization reactions by complexes **1a**, **1b**, **2** and **7** resulted in 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 (GPC) analysis of polymers gave M_n values ranging from about 17000 to 26000 Da, Table 4. The polydispersity index values (M_w/M_n = 1.5-1.9) is indicative of relatively broad molecular weight distributions, somewhat higher than what expected for controlled polymerization. This phenomenon may be attributed to side trans-esterification reactions occurring in the course of the polymerization process.[42d,43]

According to DSC measurements, the isotactically-pure polylactides obtained from L-lactide and **1a**, **1b**, **2**, **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-lactide exhibited lower T_g (43-46 °C) and no melting temperature.

Table 4. Results of L- and D,L-lactide bulk polymerizations[a]

Catalyst (g)	lactide	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	26,100	1.6	--
1a (0.040)	D,L-LA	1.37	80	46.2		25,900	1.6	0.42
2 (0.039)	L-LA	1.88	95	55.9	166.1	23,000	1.5	--
2 (0.033)	D,L-LA	1.24	86	45.2		21,000	1.7	0.54
1b (0.040)	L-LA	1.47	85	56.4	164.3	22,000	1.8	--
1b (0.040)	D,L-LA	1.32	76	43.4		18,700	1.8	0.40
7 (0.028)	L-LA	1.08	88	58.2	165.0	19,000	1.7	--
7 (0.026)	D,L-LA	0.85	77	43.2		17,000	1.9	0.63

[a] Polymerization conditions: lactide/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 ^1H homonuclear decoupled NMR analysis.

Conclusions

The straightforward synthesis of natural α-aminoacidato derivatives of Nb(V) and Ta(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 Ta-methionato species has afforded a rare example or tantalum-gold heterobimetallic complex, proving that the methionato ligand may act as effective S-donor. Moreover, a selection of Nb/Ta products have been tested as catalytic precursors for the ring opening polymerization of L-lactide and D,L-lactide. Although the niobium species revealed 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 centres, 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.

Acknowledgements

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Supporting Information Available

Figures SI1-SI3 show an expanded view of the unit cell of compounds **2**, **8** and **9**, detailing the interconnected molecules through H-bonds. The material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference numbers 918361 (**2**), 918363 (**7**), 918364 (**8**), 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, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table of Contents Synopsis

The straightforward synthesis of natural α-aminoacidato derivatives of commercial Nb(V) and Ta(V) ethoxides has been reported. The first examples of crystallographically-characterized coordination adducts of such metals bearing an aminoacidato ligand are provided.

Synopsis Artwork