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Preparation of intermetallic phases of noble metals and tin by thermolysis of metal-organic coordination polymers

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Abstract

Intermetallic phases of noble metals (Ru, Rh, Pd, Os, Ir, Pt and Au) were prepared by controlled thermolysis of coordination polymers on the basis of cyanometallates and trimethyltin units (super-prussian blue derivatives). The thermal reaction was carried out under different atmospheres: oxidizing, inert and reducing, upto 1000 °C. Under oxidizing conditions, intimate mixtures of oxides (SnO_2 with RuO_2, Rh_2O_3, IrO_2, Pt_3O_4, respectively) were obtained that could be reduced in a second step to the pure noble metals and intermetallic phases incorporating tin (Ru_3Sn_7, $RhSn_2$, $IrSn_4$, Ir_5Sn_7, $IrSn_2$, $PdSn_2$, $Pd_{20}Sn_{13}$, Pd_3Sn_2, PtSn, $PtSn_4$, Au_5Sn, AuSn were all detected). Under reducing conditions, mixtures of metals and intermetallic phases were obtained that could subsequently be oxidized by further thermal treatment to noble metals on SnO_2. This offers a new synthetic pathway to such intermetallics and to noble metals on SnO_2 supports.

Keywords: Thermolysis; Noble metals; Coordination compounds; Intermetallic compounds; X-ray diffraction

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1. Introduction

Coordination polymers of the general type $(Me_3Sn)_nM(CN)_m$ ($Me = CH_3$) present an atomic mixture of two kinds of metals that can be quite different from a chemical point of view, namely the combination of noble metals with tin. These compounds are easily available by precipitation from aqueous solutions of potassium cyanometallates $K_nM(CN)_m$ and trimethyltin chloride, e.g.

$$K_4Os(CN)_6 + 4Me_3SnCl \rightarrow (Me_3Sn)_4Os(CN)_6\downarrow + KCl \quad (1)$$

for osmium.

We have shown recently for the corresponding Fe^{II}, Fe^{III}, Co^{III}, and Ru^{II} compounds that a controlled thermolysis leads to nanocrystalline oxides and mixed oxides (under air) and metals and intermetallic phases (under inert or reducing conditions). In particular, we found α-Fe_2O_3 (nanocrystalline), SnO_2 (nanocrystalline), Co_2SnO_4, and RuO_2 (all under air) and Fe_3SnC, $FeSn_2$, Ru_3Sn_7 (all under argon or H_2/N_2) [1]. As intimate bimetallic mixtures were generally obtained, it appeared interesting to study the same reaction type with noble metals, as it is likely that intimate mixtures of metals, intermetallics and metal oxides with tin or tin dioxide will be formed upon thermolysis. A second thermal treatment of these primary reaction mixtures under either reducing or oxidizing atmosphere may lead to finely dispersed noble metals on SnO_2 (potentially interesting in heterogeneous catalysis) or to intermetallic phases of tin with these noble metals.

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The latter are difficult to obtain by conventional high-temperature syntheses from the metals. The presented thermolysis can be carried out at lower temperature due to the presence of suitable organic leaving groups like Me_3SnCN or $(CN)_2$ in the precursors [1].

2. Experimental

Fourier transform IR spectroscopy was carried out with a Perkin-Elmer PE 1720 instrument in KBr pellets. Combined thermogravimetry-differential thermal analysis (TG-DTA) was carried out on a Netzsch STA 409 system (sample mass: 50–120 mg; open alumina crucibles; 30–1000 °C; 10 K min^{-1}; dynamic atmosphere; 50 ml min^{-1}). The atmospheres were air, argon and H_2/N_2 (5:95 = V:V). The reproducibility of mass losses and gains was of the order of 1–3%, depending on the compound and the individual reaction step.

X-ray powder diffraction was carried out with a Bruker Advance D8 system on powdered or mechanically flattened (in the case of metals) samples in Bragg–Brentano mode using Cu Kα radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy was carried out on gold-sputtered samples using a Philips SEM 515 instrument operated at 25 kV.

All compounds were prepared according to standard procedures by precipitation from the potassium cyanometallates and trimethyltin chloride (Eq. (1)) [1–4]. The only exception was the gold complex that was precipitated with triethyltin bromide. All compounds were characterized by elemental analysis (C, H and N), infrared spectroscopy and X-ray powder diffraction.

3. Results and discussion

All investigated compounds are shown in Table 1. All compounds were subjected to four different programs (Fig. 1).

(A) Heating under air atmosphere to 1000 °C, then cooling under air.

(B) Heating under air atmosphere to 1000 °C, then cooling under air to 25 °C and heating again to 1000 °C under reducing atmosphere (H_2/N_2), then cooling under reducing atmosphere.

(C) Heating under reducing atmosphere ($H_2 : N_2 =$ 5:95) to 1000 °C, then cooling under reducing atmosphere.

(D) Heating under inert atmosphere (argon) to 1000 °C, then cooling under inert atmosphere to

Table 1
All investigated coordination compounds and the obtained products after different thermal treatment[a]

Starting compound	Reaction products			
	Program A: 1000 °C (air)	Program B: 1000 °C (air) followed by 1000 °C (H_2/N_2)	Program C: 1000 °C (H_2/N_2)	Program D: 1000 °C (argon) followed by 1000 °C (air)
$(Me_3Sn)_4Ru^{II}(CN)_6$	$RuO_2 + 3.55\ SnO_2$	$0.33\ Ru_3Sn_7 + 1.22\ Sn$	Ru_3Sn_7, (Ru)	$RuO_2 + SnO_2$
$(Me_3Sn)_4Os^{II}(CN)_6$	$3.38\ SnO_2$	–	$Os + 2.66\ Sn$	–
$(Me_3Sn)_3Rh^{II}(CN)_6$	$0.5\ Rh_2O_3 + 2.65\ SnO_2$	$RhSn_2 + 0.65\ SnO$	$RhSn_2$ + unknown phase ($RhSn_4$?) (formal composition $Rh + 2.13\ Sn$)	$Rh_2O_3 + 2.13\ SnO_2$
$(Me_3Sn)_3Ir^{III}(CN)_6$	$IrO_2 + 2.90\ SnO_2$	$IrSn_4$, (Ir), Sn, SnO	$Ir_5Sn_7 + IrSn_2$	Ir, (IrO_2), SnO_2
$(Me_3Sn)_2Pd^{II}(CN)_4$	$Pd + 1.73\ SnO_2$, (PdO)	$PdSn_2$, Sn, unknown phase (formal composition $Pd + 1.73\ Sn$)	$Pd_{20}Sn_{13}$, Pd, Sn (formal composition $Pd + 0.84\ Sn$)	$0.33\ Pd_3Sn_2 + 0.17\ SnO_2$, ($Sn_3O_4$)
$(Me_3Sn)_2Pt^{II}(CN)_4$	Pt_3O_4, PtSn, SnO_2, unknown phase	$PtSn_4$, Sn	$PtSn_4$, Sn,	SnO_2
$(Et_3Sn)Au^{I}(CN)_2$	$Au + 0.82\ SnO_2$	Au_5Sn + AuSn (formal composition $Au + 0.82\ Sn$)	Au_5Sn + AuSn (formal composition $Au + 0.52\ Sn$)	Au_5Sn, AuSn, SnO_2,

[a] The products were identified by X-ray powder diffractometry. Where applicable, the relative product stoichiometry (by thermogravimetry as related to the parent compound) is also given. Products in parentheses were detected only in traces.

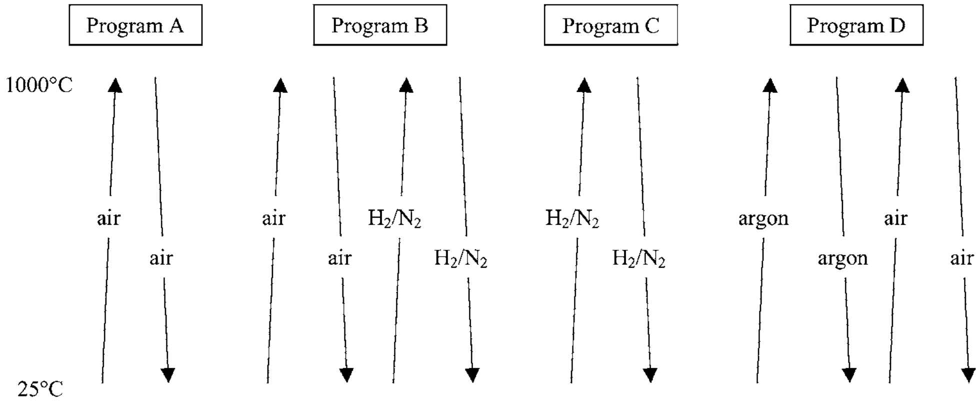

Fig. 1. Temperature programs for treatment of the samples.

200 °C, changing the atmosphere to air during cooling to 25 °C, then heating to 1000 °C under air and cooling under air.

In general, there were almost no differences between heating the initial precursor under argon or under H_2/N_2, therefore the first step in (program D) was done under inert atmosphere rather than under H_2/N_2. After thermal treatment under air, usually mixtures of oxides were obtained, whereas reducing or inert atmosphere led to metals and/or intermetallic phases. The single compounds are now discussed separately.

Some general remarks that apply to all the following compounds: All mass loss values in percent refer to the initial mass of the sample, i.e. to the intact coordination polymer. All products have been identified by X-ray diffractometry of the products using Release 1998 of the JCPDS Powder Diffraction File. Product ratios were computed using this phase information and the mass loss from thermogravimetry. Unless otherwise indicated, it was generally assumed that the noble metal did not leave the sample during annealing.

3.1. $(Me_3Sn)_4Ru^{II}(CN)_6 \cdot 2H_2O$

This coordination polymer crystallizes as dihydrate. Its structure has been determined earlier from single crystal diffraction data. The compound is isostructural with the corresponding iron(II) compound $(Me_3Sn)_4Fe^{II}(CN)_6$ [5].

Heating under air (program A) leads to a multi-step decomposition. During the first step (50–150 °C; $\Delta m = -3.5\%$), the crystal water is lost (calculated $\Delta m = -3.8\%$). Thereafter, two decomposition steps can be distinguished (220–240 °C; $\Delta m = -10.0\%$, and 240–550 °C; $\Delta m = -16.0\%$). X-ray powder diffractograms recorded both at 550 and 1000 °C indicate a partially amorphous, poorly crystalline mixture of $RuO_2 + 3.55\ SnO_2$. The ratio of ruthenium to tin was derived from the mass loss assuming that ruthenium did not leave the sample. However, given the known volatility of elemental ruthenium as RuO_4, partial loss of ruthenium cannot be excluded. Interestingly, RuO_2 cannot be prepared by direct oxidation of the metal under dynamic air atmosphere due to the volatility of the further oxidation product RuO_4.

Subsequent heating under reducing atmosphere (program B) leads to the formation of Ru_3Sn_7 and elemental Sn (30–500 °C; $\Delta m = -15.7\%$) in a ratio of $\frac{1}{3}Ru_3Sn_7 + 1.22\ Sn$ (computed mass loss for a complete reduction to the metals: $\Delta m = -15.4\%$). The ratio of ruthenium to tin is 1:3.55 (78.0 at.% Sn). According to the phase diagram of ruthenium and tin, Ru_3Sn_7 exists as a high-melting intermetallic phase (melting point ca. 1300 °C) that forms a eutectic mixture with Sn [6]. The formation of this mixture upon heating to 1000 °C is therefore, well conceivable.

If the initial coordination polymer is heated under reducing conditions (program C), again a multi-step decomposition is observed. In the first step, the crystal water is lost (50–120 °C; $\Delta m = -3.5\%$). Subsequently, a weight loss of 48.2% occurs from 220–440 °C which is followed by a slow but continuous weight loss ($\Delta m = -7.0\%$ up to 1000 °C). As products, we identified Ru_3Sn_7 and traces of elemental ruthenium. It appears likely that the continuous weight loss is due to slow evaporation of ruthenium as RuO_4. If we neglect this effect, we can compute a composition of the product of Ru + 2.45 Sn. For a reaction to pure Ru_3Sn_7 with Ru:Sn = 1:2.33, we would expect a mass loss of $\Delta m = -60.1\%$ that compares well with the observed value ($\Delta m = -58.7\%$). We conclude that the product consists mostly of the intermetallic phase Ru_3Sn_7. Conventionally, this phase can be prepared by heating the elements in a closed quartz tube to 1200–1500 °C for 20 min [7].

If this reaction product is heated again under air (program D), oxidation to a mixture of RuO_2 and SnO_2 occurs (200–1000 °C). However, this appears to be not quantitative as the observed value of $\Delta m = +8.1\%$ is considerably lower than the computed one of $\Delta m = +11.7\%$ (for "Ru + 2.45 Sn").

3.2. $(Me_3Sn)_4Os^{II}(CN)_6$

According to powder diffraction, this compound is isostructural with the corresponding Fe^{II} and Ru^{II} compounds [5].Decomposition under air leads to a first mass loss from 220 to 500 °C ($\Delta m = -42.2\%$), followed by a slow but continuous mass loss ($\Delta m = -6.9\%$ upto 1000 °C). As reaction product, only SnO_2 was obtained (3.38 SnO_2 according to the mass loss). Apparently, all osmium has left the sample as volatile OsO_4.

Decomposition under reducing conditions prevents the formation of osmium tetroxide. We observed a single-step mass loss from 240 to 610 °C with $\Delta m = -49.5\%$. As products, elemental osmium and tin were observed (Os + 2.66 Sn). The phase diagram of osmium and tin is not known [6]. However, it has been reported that these elements do not mix in the liquid phase [7]. Only at high pressure (7.7 GPa) and high-temperature (627–1327 °C), an intermetallic phase Os_3Sn_7 can be prepared [8]. Due to the easy formation and high volatility of OsO_4, a further experiment subjecting this Os/Sn mixture to heating under air appeared unnecessary.

3.3. $(Me_3Sn)_3Rh^{III}(CN)_6$

This compound is isostructural with the corresponding cobalt(III) and iron(III) complexes [9], $(Me_3Sn)_3Co^{III}(CN)_6$ and $(Me_3Sn)_3Fe^{III}(CN)_6$, as a comparison of the powder diffractograms shows.

Heating the rhodium complex under air (program A) leads to a two-step reaction. The first step ranges from 100 to 380 °C ($\Delta m = -33.5\%$) and leads to an amorphous product with small X-ray reflections of RhO. In the second step from 380 to 650 °C, the mass increases again by $\Delta m = +3.6\%$. This can be ascribed to further oxidation of rhodium(II) to rhodium(III) as shown by the product analysis: 0.5 Rh_2O_3 + 2.65 SnO_2. The temporary occurrence of RhO is unusual as this oxide cannot be prepared by direct oxidation of the metal but only by thermal decomposition of Rh_2O_3 [10]. Rhodium(III)oxide is the usual end product of oxidation of rhodium under air [11].

If this product is subjected to heating under reducing atmosphere (program B), a further mass loss of $\Delta m = -14.2\%$ is observed from 200 to 900 °C. Reduction to $RhSn_2$ and 0.65 SnO_2 has occurred as shown by X-ray diffractometry (calculated $\Delta m = -18.7\%$).

Under reducing atmosphere (program C), the decomposition of the coordination polymer occurs from 140 to 450° with a mass loss of 52.6%. By diffractometry, $RhSn_2$ and small amounts of a hitherto unknown phase can be detected already at 500 °C (both with broad diffraction peaks) and at 1000 °C (with narrow diffraction peaks). If we assume that the product contains only rhodium and tin, we compute a composition of Rh + 2.13 Sn (68.1 at.% Sn), indicating that most of the sample probably consists of $RhSn_2$. A view on the Rh–Sn phase diagram [12] shows that for the given composition, a mixture of $RhSn_2$, Sn and potentially $RhSn_4$ is expected [6]. The structure of $RhSn_4$ is not known. Conventionally, $RhSn_2$ can be prepared by melting the metals together around 1000 °C [13–15]. If this sample is heated up again under air (program D), oxidation to 0.5 Rh_2O_3 + 2.13 SnO_2 leads to an increase in mass of 13.8% (30–1000 °C; calculated: +12.3%).

3.4. $(Me_3Sn)_3Ir^{III}(CN)_6$

A comparison of powder diffraction data suggests the same structure as the homologous cobalt(III), iron(III) and rhodium(III) compounds [9].

As with the rhodium complex, thermolysis under air (program A) first leads to an amorphous product

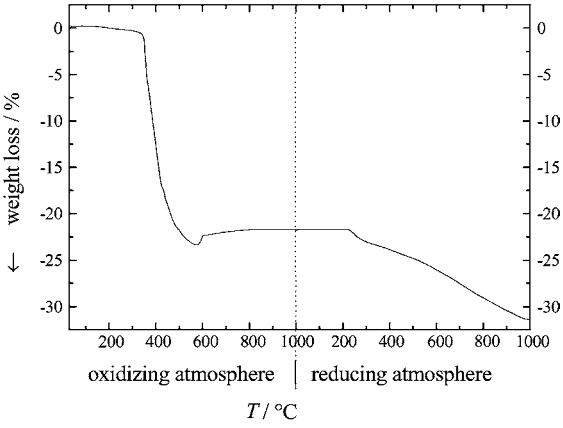

Fig. 2. Thermogravimetric data for heating of the iridium complex $(Me_3Sn)_3Ir^{III}(CN)_6$ first under air and then under reducing atmosphere (H_2/N_2).

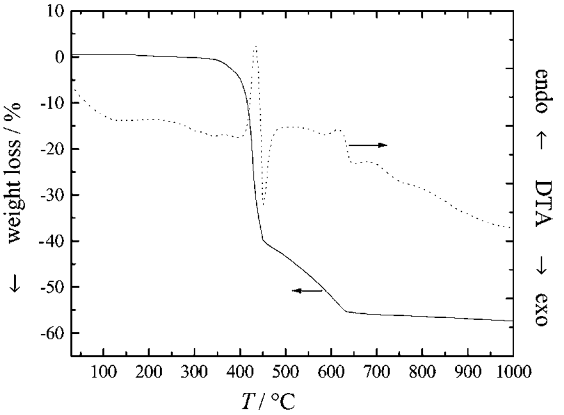

Fig. 3. Thermogravimetric data for heating of the iridium complex $(Me_3Sn)_3Ir^{III}(CN)_6$ under reducing atmosphere (H_2/N_2).

(300–580 °C; $\Delta m = -23.0\%$) that is oxidized again (580–800 °C; $\Delta m = +1.7\%$). The final product consists of crystalline $IrO_2 + 2.90\ SnO_2$. Iridium dioxide is the usual oxidation product of iridium [16] that can also prepared by hydrolysis and subsequent calcination of $IrCl_3$ [17]. Remarkably, no solid solution of SnO_2 and IrO_2 (both crystallizing in the tetragonal rutile type) was observed. Such mixed crystals can be prepared by sol–gel synthesis followed by calcination at 450 °C [18].

Heating this product again to 1000 °C under reducing atmosphere (program B) leads to a mixture of Sn, SnO, $IrSn_4$ and traces of elemental iridium (200–1000 °C; $\Delta m = -14.6\%$, calculated for reduction to "Ir + 2.90Sn": $\Delta m = -14.8\%$). Fig. 2 shows the consecutive TG curves recorded first under oxidizing and then under reducing atmosphere.

Under reducing atmosphere (program C), heating of the coordination polymer results in a mass loss of $\Delta m = -57.7\%$ (350–650 °C). The product is amorphous at 650 °C and crystalline at 1000 °C. Weak X-ray reflections of Ir_5Sn_7 and strong reflections of $IrSn_2$ (CaF_2 structure type) are detected. Conventionally, Ir_5Sn_7 and $IrSn_2$ are prepared from the elements at 980 °C [7,15,19]. The phase diagram of Ir–Sn is not known [6]. Fig. 3 shows the TG-DTA curve for heating the iridium complex under H_2/N_2.

Oxidation of this product (program D) leads to SnO_2, elemental iridium and traces of IrO_2. The increase in mass of $\Delta m = +7.1\%$ (30–1000 °C) is much smaller than that expected for a full oxidation to $Ir + 2SnO_2$ ($\Delta m = +14.9\%$). This may be related to a loss of iridium at higher temperature (like rhodium dioxide, IrO_2 is also volatile at high-temperature under air as IrO_3).

3.5. $(Me_3Sn)_2Pd^{II}(CN)_4$

This complex is isostructural to the corresponding nickel polymer $(Me_3Sn)_2Ni(CN)_4$ [20] as indicated by powder diffraction data.

Heating under air (program A) leads to a mass loss of $\Delta m = -36.2\%$ (260–360 °C amorphous product), followed by a gain in mass of $\Delta m = +4.5\%$. As products, we identified Pd, SnO_2 and traces of PdO. If we neglect the small content of PdO, a product composition of $Pd + 1.73\ SnO_2$ can be computed. Fig. 4 shows the TG curve for heating the palladium complex under air.

Further heating under reducing conditions (program B) leads to a mass loss of $\Delta m = -11.1\%$ (200–1000 °C). As products, we found $PdSn_2$, elemental Sn and an unidentified phase. The computed mass loss for a full reduction to Pd and 1.73 Sn is $\Delta m = -10.4\%$, i.e. it is likely that the unidentified phase also consists of an intermetallic compound of Pd and Sn. The elemental ratio of Pd to Sn is 1:1.73, i.e. the molar fraction of Sn is 63.4%. The phase diagram shows that $PdSn_2$ decomposes peritectically at 600 °C to Sn and PdSn [6]. It can be prepared from the elements at around 1000 °C [13].

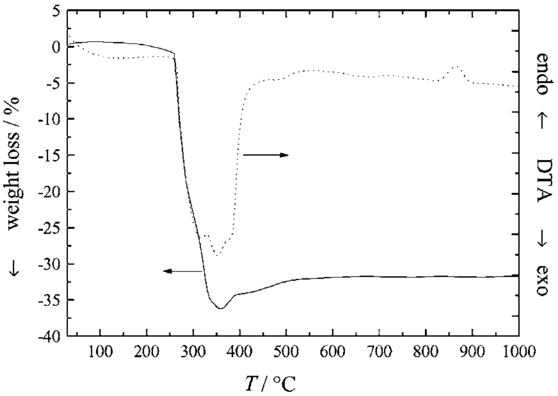

Fig. 4. Thermogravimetric data for heating of the palladium complex $(Me_3Sn)_2Pd^{II}(CN)_4$ under air.

Heating $(Me_3Sn)_2Pd(CN)_4$ under reducing conditions (program C) results in a single-step decomposition (250–400 °C; $\Delta m = -61.7\%$). As products, elemental Pd and Sn and the intermetallic phase $Pd_{20}Sn_{13}$ were identified. The latter can be prepared conventionally from the elements above 1000 °C, followed by quenching [21]. It decomposes peritectically above 900 °C [6]. If only metals are present, a ratio of Pd to Sn of 1:0.84 is computed (45.7 at.% Sn).

Subsequent oxidation under air (program D) results in a mass increase of $\Delta m = +1.2\%$ from 300 to 1000 °C with Pd_3Sn_2 and SnO_2 as reaction products. The computed mass change corresponds well with that computed for the partial oxidation of "Pd + 0.84 Sn" to $\frac{1}{3}Pd_3Sn_2 + 0.17\ SnO_2$. The compound Pd_3Sn_2 can be prepared conventionally from the elements in the melt at around 1000 °C [13].

3.6. $(Me_3Sn)_2Pt^{II}(CN)_4$

The structure of this coordination polymer appears to be different from the lower homologous as the powder diffractogram strongly differs from those of the nickel(II) and the palladium(II) compounds.

Heating under air to 1000 °C (program A) results in a single-step decomposition (100–220 °C; $\Delta m = 93.1\%$) with a solid residue consisting of SnO_2, Pt_3O_4, PtSn and an unknown phase. Surprisingly, this mass loss is much higher than expected, so that only a fraction of the initial platinum and tin content can be still present. The nature of the volatile platinum species is not known. Subsequent heating under reducing atmosphere (program B) leads to a mixture of $PtSn_4$ and Sn (480–1000 °C; $\Delta m = +1.2\%$). $PtSn_4$ decomposes peritectically above ca. 520 °C [6].

Heating the coordination polymer under reducing atmosphere (program C) leads to a similarly high mass loss of $\Delta m = -95.8\%$ (80–220 °C) with elemental Sn and small amounts of $PtSn_4$ as products. Subsequent heating under air (program D) leads to a mass change of $\Delta m = +0.6\%$ (30–1000 °C) and SnO_2 as the only safely detectable crystalline product.

3.7. $(Et_3Sn)Au^{I}(CN)_2$

Heating the gold complex under air (program A) results in a single-step mass loss of $\Delta m = -29.6\%$ (220–500 °C) with elemental gold and SnO_2 as products. The product ratio can be computed to $Au + 0.82\ SnO_2$. Subsequent reduction (program B) leads to a mixture of Au_5Sn (major phase) and AuSn (30–1000 °C; $\Delta m = -4.9\%$, calculated for full reduction: $\Delta m = -5.7\%$). The molar ratio of Au to Sn is 1:0.82, i.e. the fraction of Sn is 45.1 at.%. These intermetallic phases can be prepared conventionally from the elements by annealing [22]. The phase diagram of gold with tin shows that AuSn and Au_5Sn are two peritectically decomposing intermetallic compounds that would be expected for the given composition after cooling besides elemental gold [6,23]. However, the presence of elemental gold can be definitely excluded by X-ray diffraction.

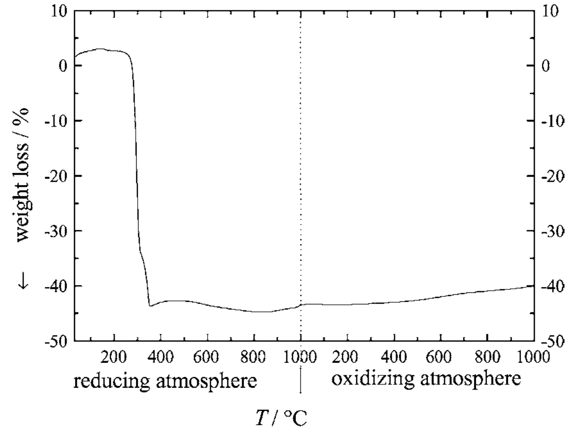

Fig. 5. Thermogravimetric data for heating of the gold complex $(Et_3Sn)Au^{I}(CN)_2$ first under reducing atmosphere (H_2/N_2) and then under air.

Heating the coordination polymer under reducing atmosphere (program C) leads to a single-step mass loss (250–350 °C; $\Delta m = -43.0\%$) and the same intermetallic compounds Au_5Sn and AuSn. From the mass loss, a molar ratio of gold to tin of 1:0.52 can be computed (34.2 at.% Sn). Further heating under air (program D) leads to partial oxidation ($\Delta m = +2.8\%$ from 400 to 1000 °C) and a mixture of SnO_2, AuSn and Au_5Sn. Fig. 5 shows the thermogravimetric data for the gold complex heated first under H_2/N_2 and then under air.

4. Conclusions

Bimetallic coordination polymers that consist of tin and a noble metal are suitable precursors to intermetallic phases. The nature and composition of the products depends on the specific case and on the affinity of the noble metal to tin. Most reactions are finished around 500 °C therefore, these reactions may offer suitable alternatives to conventional high-temperature metallurgical syntheses. However, the fact that often mixtures are obtained may prevent a synthetic application to some degree. Further thermal treatment of the products can lead to noble metals or noble metal oxides on tin dioxide supports.

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