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On the formation of M^{2+}-Sb^{3+}-alkoxide precursors and sol–gel processing of M–Sb oxides with M=Cr, Mn, Fe, Co, Ni, Cu and Zn

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Binary alkoxide complexes of compositions close to $MSb(OEt)_5$, with M = Mn, Fe, Co and Ni, have been prepared and characterized by their i.r. and u.v.–VIS spectra, while Cr, Cu and Zn do not form similar ethoxide complexes with $Sb(OEt)_3$. The Mn and Fe complexes must be prepared in inert atmosphere as they are very easily oxidized. The Fe complex is metastable and decomposes within a few hours. The Co complex can only be prepared in the presence of acetonitrile. X-ray amorphous gels were formed upon hydrolysis of solutions containing M to Sb species in the ratio 1:2 for M = Mn, Fe, Co and Ni. The gels consisted of agglomerated particles of sizes from 75 to 300 nm. The decomposition of the gels in air and in nitrogen has been monitored by means of thermogravimetric measurements. Samples of heated gels were quenched from various temperatures in the region 50–950 °C, and the formed oxides were characterized by their X-ray powder patterns and by their infrared spectra. At 950 °C MSb_2O_6 was formed in air, while in nitrogen MSb_2O_4 (M = Mn, Co and Ni) was formed at intermediate temperatures. At higher temperatures the latter compound decomposed and Sb_2O_3 sublimated.

1. Introduction

The sol–gel process has attracted much interest during recent years, in connection with the preparation of new oxide materials. The process involves the use of molecular precursors, inorganic or organic. Multicomponent systems can be studied by mixing solutions containing different molecular precursors. The use of metal alkoxides as precursors in organic solvents offers special advantages over the use of inorganic salts as precursors in water as solvent, in that the hydrolysis–condensation reactions can be more easily controlled. Most low-valency transition metal alkoxides are insoluble in nearly all organic solvents. Binary alkoxide complexes containing at least one transition-metal atom are, however, soluble to a greater extent. In this article we report on the possibility of preparing soluble binary alkoxide complexes of M^{2+}–Sb^{3+} ethoxides with M = Cr, Mn, Fe, Co, Ni, Cu and Zn. The complexes formed have been characterized by their infrared (i.r.) and ultraviolet (u.v.–VIS) spectra. They have been used as precursors in sol–gel processing of MSb oxides with an M:Sb ratio of 1:2. The gels, formed via hydrolysis reactions, have also been studied and characterized by their i.r. spectra and by their X-ray powder diffractograms (XRD). The sizes of the particles formed and the element distribution have been determined in a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). Finally the decomposition of the gels upon heating in inert atmosphere or in air has been monitored by thermogravimetric analysis (TGA). The binary oxides formed have been characterized by their X-ray powder diffractograms and i.r. spectra, and by SEM studies.

2. Experimental procedure

2.1. Reagents

The following starting materials were used in this study for the preparation of $MSb_x(OEt)_{2+3x}$ alkoxide precursors with M = Cr, Mn, Fe, Co, Ni, Cu and Zn. Anhydrous $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$ of p.a. quality were used. $CrCl_2$ was washed with tetrahydrofuran (THF) in order to ensure that the reagent was free from $CrCl_3$. All solvents were of p.a. quality and were dried prior to use. The ethanol was dried with CaH_2 and/or molecular sieves (0.3 nm), toluene and hexane with Na, while molecular sieves were used to dry the acetonitrile and nujol solvents. The latter was needed in connection with the i.r. studies. In order to ensure that the solvents did not contain any dissolved oxygen, which could cause oxidation of some of the complexes formed (see below), the solutions were degassed and then saturated with nitrogen.

2.2. Preparation of M- and Sb-ethoxides

$Sb(OEt)_3$ was prepared from $SbCl_3$ using the ammonia route [1] and purified by distillation in vacuum, and Na(OEt) was obtained by dissolving an appropriate amount of Na in ethanol. $Zn(OEt)_2$ was prepared by adding $Zn(Et)_2$ (dissolved in hexane) to

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ethanol [2]. $M(OEt)_2$ with M = Cr, Mn, Fe, Co, and Cu were synthesized according to the lithium route [3]. The solid materials thus formed were washed several times with ethanol and centrifuged in order to ensure that all the LiCl formed had been removed.

2.3. Preparation of $MSb_x(OEt)_{2+3x}$ complexes

Three different routes were used to prepare the $MSb_x(OEt)_{2+3x}$ complexes. Various M:Sb ratios have been tested in order to evaluate the extent to which more than one type of $MSb_x(OEt)_{2+3x}$ complex can be formed for $x \leqslant 2$. The reactions were carried out in a glove box in an atmosphere free from oxygen and water vapour, normally at room temperature; but in some cases temperatures up to 60 °C were used to speed up the reactions. Preparation route 1 involved the following reactions

$$2Na(OEt) + xSb(OEt)_3 \rightarrow xNaSb(OEt)_4 + (2-x)NaOEt$$

$$MCl_2 + xNaSb(OEt)_4 + (2-x)Na(OEt) \rightarrow MSb_x(OEt)_{2+3x} + 2NaCl_{(s)}$$

The reactions were performed in an 80:20 (vol %) mixture of toluene and ethanol.

Reaction route 2 implied that appropriate amounts of $M(OEt)_2$ and $Sb(OEt)_3$ were mixed using the same solvent as in route 1. The M–Sb complexes generally took longer to form, probably due to the lower solubility of the M ethoxides in the toluene–ethanol mixture.

The Co–Sb complex could not be prepared via routes 1 or 2, but if a mixture of 80:20 (vol %) of acetonitrile and toluene was used $Co(OEt)_2$ dissolved. This led us to investigate to what extent the other M–Sb complexes could be formed according to

$$M(OEt)_2 + xSb(OEt)_3 \rightarrow MSb_x(OEt)_{2+3x}$$

using a solvent consisting of an 80:20 mixture of CH_3CN and toluene.

2.4. Formation of gels

Almost transparent gels were formed within 12 h when the solutions containing the various M–Sb complexes were exposed to atmospheric humidity. In the presence of oxygen, the Mn^{2+} and Fe^{2+} ions in the M–Sb complexes were rapidly oxidized to the M^{3+} state. In order to avoid oxidation, the gelling of the solutions containing these complexes was performed by exposing them to a humidified nitrogen atmosphere. An antimony oxide gel was prepared by hydrolysis of a toluene solution containing $Sb(OEt)_3$. The gels were characterized by XRD, by i.r. spectra and by SEM studies.

2.5. Formation of M–Sb oxides

The formation of the various M–Sb oxides upon heating the gels was monitored in a TG unit. The gels and the intermediate and end products formed on the heat treatment were characterized by their X-ray powder photograms, by their i.r. spectra and by SEM studies.

2.6. Characterization

The FT–I.R. spectra were recorded in a Polaris spectrometer equipped with a DTGS detector covering the frequency range 400–4000 cm^{-1}. The spectra of solid materials were recorded with use of KBr tablets. Normally the various solutions were evaporated to dryness and the precipitates were dissolved in nujol. In these cases a KBr sample cell was used in recording the spectra. The u.v.–VIS spectra were recorded in a Philips PU 8740 spectrometer covering the wavelength range 200–900 nm (50–11.1 kK) with use of a quartz cell.

The X-ray powder photographs were recorded in a Guinier–Hägg focusing camera, using $CuK_{\alpha 1}$ radiation, and with Si as internal standard.

The TG analyses were performed in a Perkin–Elmer TG-2 unit. The measurements were carried out in nitrogen atmosphere and in air at 50–950 °C. A heating rate of 5° min^{-1} was used.

The oxide powders and dried gels obtained have been characterized with respect to particle sizes and element distribution in an SEM (Jeol 820) equipped with an energy dispersive spectrometer (Link AN 10000). The micrographs presented below were obtained with use of secondary electrons.

3. Results

None of the preparation routes described above yielded a binary M^{2+}–Sb^{3+} alkoxide complex for M = Cr^{2+}. With M = Cu and Zn, most of the MCl_2 reacted to form the insoluble compounds $Cu(OEt)_2$ and $Zn(OEt)_2$ when reaction route 1 was applied. In the case of M = Cu a faintly blue solution was formed, and subsequent SEM studies of the dried gels formed by hydrolysis of this solution indicated that the Cu/Sb ratio in the solution was of the order 1:9. The X-ray powder pattern of the Cu-containing gel heat-treated up to 950 °C in air in the TG unit, showed that $CuSb_2O_6$ was formed besides Sb_2O_4. For M = Zn a transparent solution was formed, and the SEM studies of the dried gel showed that the Zn:Sb ratio in the solution was approximately 1:9. Heat treatment of this gel at elevated temperatures yielded Sb_2O_4 and $ZnSb_2O_6$. Applying routes 2 and 3 yielded similar results. Binary M^{2+}–Sb^{3+} complexes could be formed with M = Mn, Fe, Co and Ni. The formation and characterization of each M–Sb complex and of the gels formed by hydrolysis of the complexes, as well as studies of the thermal decomposition of the gels, will be described below. For comparison, corresponding studies of the Sb ethoxide, the Sb gel and the thermal decomposition of this gel will also be presented.

3.1. Formation and characterization of $Sb(OEt)_3$

In order to establish that the various M–Sb complexes had been formed, and in order to understand the thermal decomposition of the various M–Sb gels, it was necessary to characterize $Sb(OEt)_3$ and the Sb gel by their i.r. spectra and to study the thermal decomposition of the Sb gel. The Sb ethoxide, prepared as described above, was dissolved in nujol, and the i.r. spectrum was recorded. As seen in Fig. 1 the spectrum contains absorption peaks typical for alkoxides in the region 1150–850 cm^{-1}. Besides these peaks, one band consisting of two superimposed peaks can be found in the region 650–400 cm^{-1}, with peaks at 586 and 550 cm^{-1}. These peaks are ascribed to the Sb–O bonds. Our findings are in agreement with those reported in Reference 4.

3.1.1. *Formation and characterization of the Sb gel*

The Sb gel was prepared by exposing a toluene solution of $Sb(OEt)_3$ to air. The gelling process was normally finished within 48 h, and the product consisted either of small, almost transparent pieces or of powder. The X-ray powder pattern of the gel showed that the senarmontit modification of Sb_2O_3 had been formed. The i.r. spectrum of the gel exhibited peaks at 954 and 735 cm^{-1}, which could be ascribed to senarmontit, and peaks around 604 and 460 cm^{-1}. The latter probably originate from amorphous antimony oxide or hydroxide.

3.1.2. *Thermal decomposition of the Sb gel, and characterization of the compounds formed*

The thermogram of the Sb gel heat-treated up to 950 °C in air is given in Fig. 2. The weight loss up to approximately 100 °C is most probably due to the transformation of residual amounts of amorphous antimony hydroxide to Sb_2O_3. This weight loss has been found to vary between different preparations and with the time the gels have been aged. According to the X-ray analysis, Sb_2O_3 is present up to 500 °C, and Sb_2O_4 above 600 °C. However, according to the weight increase observed between 500 and 600 °C, all antimony can not occur as crystalline Sb_2O_3 at 500 °C. The TG curve can be satisfactorily explained by the following reaction, however:

$$Sb_2O_4{*}Sb_2O_3 + 0.5O_2 \rightarrow 2Sb_2O_4$$

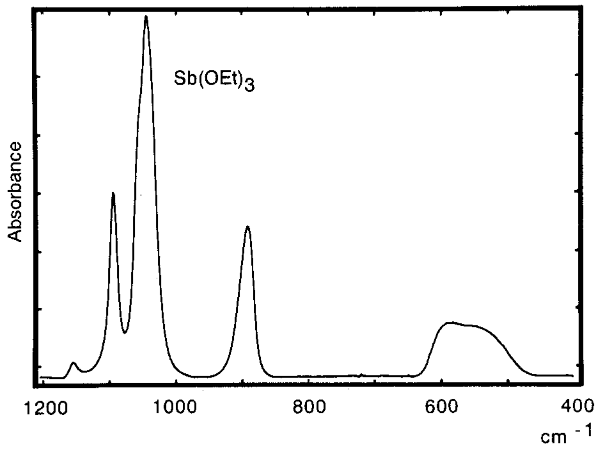

Figure 1 i.r. Spectrum of $Sb(OEt)_3$ in nujol. The nujol peak has been omitted.

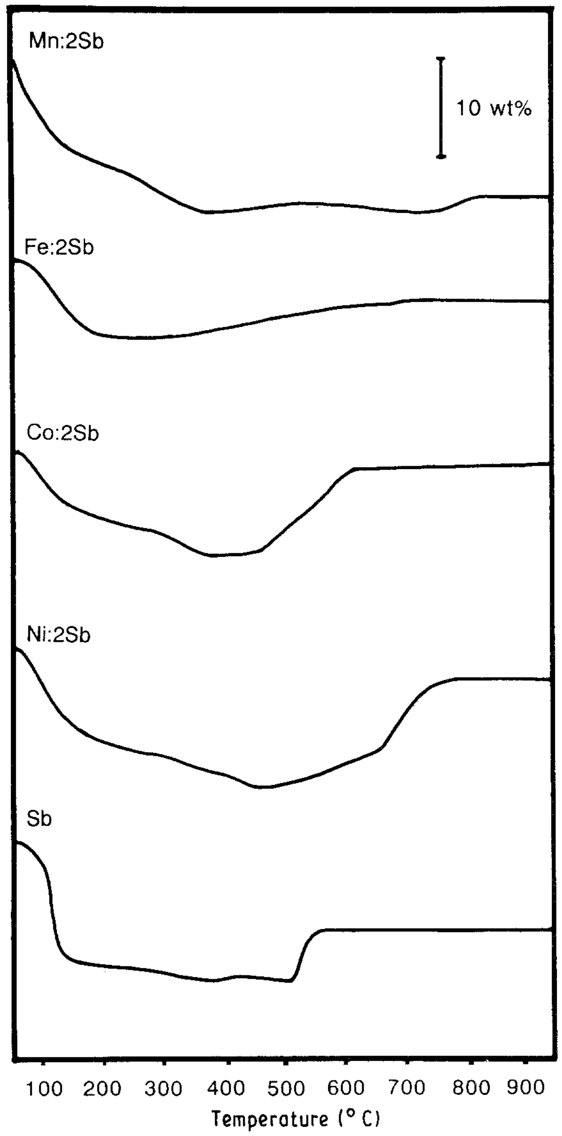

Figure 2 TG curves for Sb and MSb_2 gels heated in air with 5 K min^{-1} from 50 to 950 °C.

It must be pointed out that we do not have any X-ray or i.r. evidence for the occurrence of a crystalline phase of the composition $Sb_2O_4{*}Sb_2O_3$, but the TG curve and the X-ray analysis suggest that at 500 °C approximately 50% of the antimony content occurs as an amorphous phase of a composition close to Sb_2O_4. The thermal decomposition of the Sb gel in nitrogen atmosphere is illustrated in Fig. 3. In this case, the weight loss up to 100 °C was almost negligible, implying that this gel contained only minor amounts of antimony hydroxide. According to the thermogram, Sb_2O_3 starts to sublime around 500 °C when heat-treated in nitrogen atmosphere.

3.2. Formation and characterization of the Mn–Sb alkoxide complex

The formation of Mn–Sb alkoxide complex seemed to proceed according to the reaction equation described

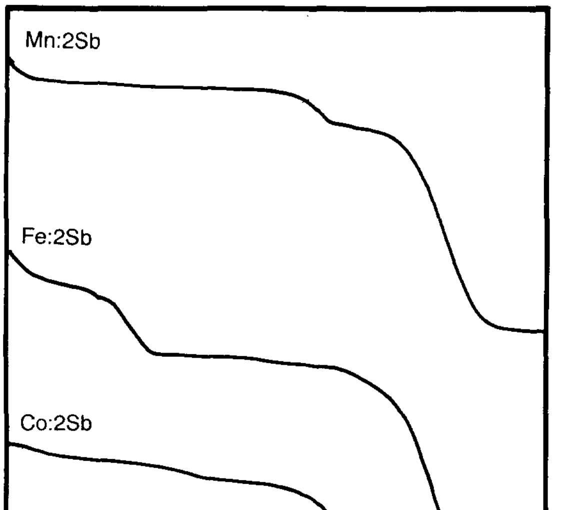

Figure 3 TG curves for Sb and MSb_2 gels heated in nitrogen with $5\ K\ min^{-1}$ from 50 to 950 °C.

in connection with preparation route 1 above. Subsequent SEM studies of gels (see below) indicated that the alkoxide solution contained less than 0.5 wt % NaCl. Preparation routes 2 and 3 could also be applied. These reaction routes seemed to be much slower than the first one. In the following we will describe the properties of the compounds formed via route 1. The results described below are, in all essential parts, also valid for materials prepared according to routes 2 and 3.

We have tried to prepare Mn–Sb alkoxides with various Mn:Sb ratios. These solutions were evaporated to dryness and the residues were dissolved in nujol prior to the recording of the i.r. spectra. The spectra of the compositions $MnSb_x(OEt)_{2+3x}$ with $x = 1$ and 2 are given in Fig. 4. A comparison of these spectra and that of $Sb(OEt)_3$ (Fig. 1) suggests that all Mn–Sb alkoxide solutions contain the same type of complex. In this connection it can be mentioned that the i.r. spectrum for $x = 0.5$ was identical with that for $x = 1$. Accordingly, during the preparation of this solution, not only NaCl but also $Mn(OEt)_2$ precipitated from the solution. The u.v.–VIS spectra of the solutions with $x = 1$ and 2 are quite similar, as seen in Fig. 5, indicating that the two solutions contain the same type of complex. By vacuum evaporation of the solvent, needle-shaped pink crystals up to 5 mm in length were formed for $x = 1$. Element analysis of these crystals showed that they contained nearly equimolar amounts of Mn and Sb. Evaporation of the solution with $x = 2$ yielded a plastic bulky material. Gentle evaporation of the same solution yielded small crystals of the same composition as above. These observations, and the findings in connection with the decomposition of the gels (see below), seem to indicate that only one type of complex is formed, independently of the overall composition of the solution with respect to the Mn to Sb content, and that this complex in the solution has a composition close to $MnSb(OEt)_5$ (see below). To what extent this complex is monomeric or polymeric is not known.

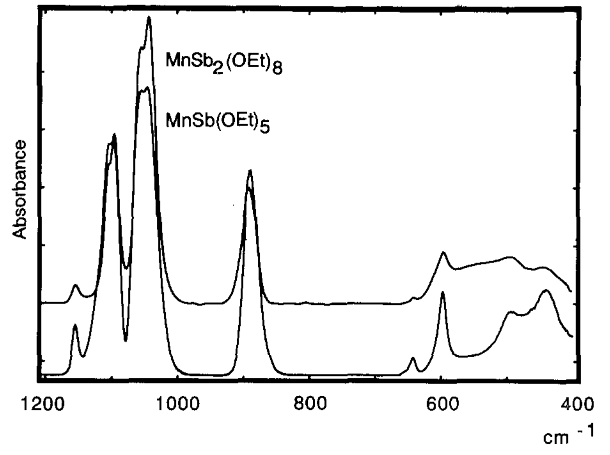

Figure 4 I.r. spectra of a nujol solution of $MnSb(OEt)_5$ and $MnSb_2(OEt)_8$. The nujol peak has been omitted.

The i.r. spectrum of the $MnSb(OEt)_5$ solution given in Fig. 4 exhibits absorption peaks typical for ethoxy groups in the region ($1150–850\ cm^{-1}$), namely two doublets and one single peak at 1105 and $1097\ cm^{-1}$, at 1060 and $1044\ cm^{-1}$ and at $890\ cm^{-1}$. In the Mn–O and Sb–O region, we observe peaks at 644, 597, 490 and $440\ cm^{-1}$. As none of these peaks is found in the spectrum of $Sb(OEt)_3$ (see Fig. 1), these peaks are ascribed to the Mn–Sb alkoxide complex. It can also be noted that this spectrum does not contain any peak which can be ascribed to the occurrence of molecules containing $-OH$ groups.

The pink solution containing the Mn–Sb–alkoxide complex was very easily oxidized by air, whereby it turned brown. The u.v.–VIS spectrum of this brown solution showed a strong charge transfer component. The u.v.–VIS spectrum of the pink solution contained a weak charge transfer component but the absorption peaks at 27.5, 23.3, 21.2 and 18.6 kK could be resolved (see Fig. 5). If octahedral symmetry is assumed (the high energy of the peaks at 21.2 and 18.6 kK seem to exclude T_d symmetry) these peaks can be associated with the following transitions; (i) the one at 27.5 kK with ${}^4T_{2g}(D) \leftarrow {}^6A_{1g}$; (ii) the one at 23.3 kK with ${}^4A_{1g}(G) \leftarrow {}^6A_{1g}$ and ${}^4E_g(G) \leftarrow {}^6A_{1g}$; (iii) the one at 21.2 kK with ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$; (iv) and finally the one

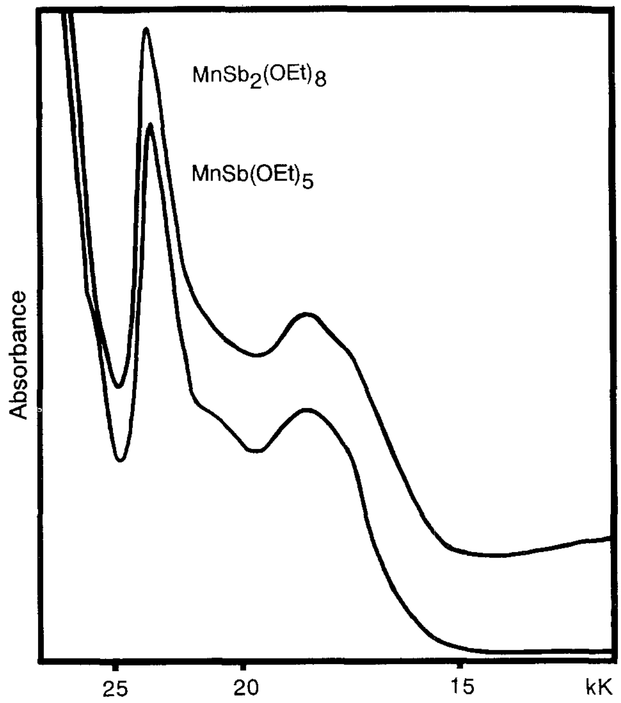

Figure 5 UV–VIS spectra of a toluene/ethanol solution of $MnSb(OEt)_5$ (lower) and $MnSb_2(OEt)_8$ (upper).

at 18.6 kK with ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$. These energies are somewhat lower than those reported for $Mn(OEt)_2$ [5] which possesses octahedral symmetry, implying that the ligand field in the Mn–Sb–alkoxide complex is weaker than that in $Mn(OEt)_2$. As discussed above, the i.r. spectrum does not contain any OH absorption band, implying that the Mn^{2+} ions are coordinated entirely by ethoxy groups.

3.2.1. Formation and characterization of Mn–Sb gels

The gelling of a toluene/ethanol Mn–Sb–alkoxide solution with $x = 2$ was accomplished by exposing the solution to a humidified nitrogen atmosphere. An almost transparent, X-ray amorphous gel was formed. The i.r. spectrum of the gel showed absorption peaks associated with –OH groups and smaller peaks arising from ethoxy groups. The spectrum is, however, completely dominated by peaks at 728, 680, 595 and 544 cm^{-1} associated with Mn–O and Sb–O bonds. Gels of solutions with $x = 2$ yielded an i.r. spectrum indicating that the excess of Sb in the solution ought to occur as antimony oxide or hydroxide in the gel (see above). It can also be noted that the i.r. spectrum did not contain any peaks which could be ascribed to toluene, implying that all toluene had evaporated during the gelling process. A micrograph of the gel is shown in Fig. 6, which shows that the gel is composed of aggregated 130–200 nm particles. Due to their small size, it has not been possible to determine the chemical composition of the individual particles. The overall Mn:Sb ratio was, however, close to 1:2.

Gels used for thermal decomposition in air were prepared by exposing the Mn–Sb alkoxide solution to air. A dark brown gel composed of agglomerates of particles. The sizes of these particles ranged from 100 to 200 nm. According to the i.r. spectrum the gel contained only small amounts of solvents and H_2O, and it exhibited a broad peak in the Mn–O and Sb–O band region with a maximum at 603 cm^{-1}.

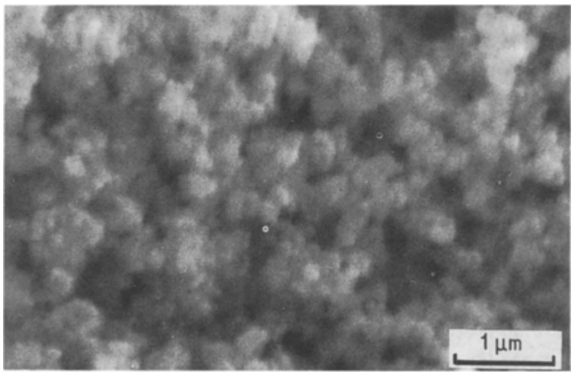

Figure 6 SEM micrograph of the MnSb gel.

3.2.2. Thermal decomposition of the Mn–Sb gel, and characterization of the compounds formed

The thermogram of the gel obtained from an Mn–Sb solution with $x = 2$, heat-treated in nitrogen atmosphere up to 950 °C with 5 K min^{-1} in the TG unit, is given in Fig. 3. X-ray powder diffractograms were taken for samples quenched from 400, 620 and 950 °C. The diffractogram of the material quenched from 400 °C exhibited weak reflections which could be ascribed to valentinit and senarmontit, two modifications of Sb_2O_3. This implies that most of the material is still X-ray amorphous at 400 °C. The X-ray analysis of the light green powder formed after heat treament up to 620 °C showed that $MnSb_2O_4$ [6] had been formed. The weight loss above 620 °C is most probably associated with decomposition of $MnSb_2O_4$ and sublimation of Sb_2O_3. This interpretation is supported by the observation that the diffractogram of material heat-treated to 950 °C exhibited weak reflections which could be ascribed to Sb_2O_3 (valentinit) and further reflections which could not be ascribed to any known phase(s). Assuming that all amorphous material had transformed into crystalline $MnSb_2O_4$ at 620 °C, the observed weight loss (14%) up to this temperature agrees rather well with the approximate composition $MnSb_2(OH)_8$ of the gel. The decomposition between 400 and 600 °C would then be associated with the following reaction:

$$MnSb_2O_2(OH)_4 \rightarrow MnSb_2O_4 + 2H_2O$$

The thermogram of the gel heat-treated in air is also shown in Fig. 2. The X-ray analysis of samples quenched from various temperatures up to 530 °C showed that the material was essentially X-ray amorphous up to this temperature, as only a few unidentified weak and diffuse reflections were present. The diffractogram of samples quenched from 950 °C contained sharp reflections which, however, could not be ascribed to any known phase(s). Prolonged heat treatment at 950 °C yielded, however, the β modification of $MnSb_2O_6$ [7].

3.3. Formation and characterization of the Fe–Sb ethoxide complex

A green solution resulted when the preparation route 2 was applied for $x = 0.5$, 1 and 2. Simultaneously, however, a small amount of a black precipitate was formed. The decanted green solution darkened within 4–5 h, and a black precipitate was formed. The charge transfer component of u.v.–VIS spectra of solutions stored for different times increased with the time of storage. This behaviour suggests that, to the extent that an Fe^{2+}–Sb^{3+}-complex is formed, the Fe^{2+}-ions in this complex are very easily oxidized to Fe^{3+} yielding an insoluble compound. Whether the oxidation occurs via an internal redox reaction, or the very low partial pressure of oxygen present in the dry box is still high enough to cause an oxidation, is not known, but the former possibility seems more probable. In this connection it can be noted that when the green solution is exposed to air, it turns to yellow. The exposure to air probably oxidizes all Fe^{2+} to Fe^{3+}. The same type of reaction was observed when preparation route 3 was applied, while route 1 yielded a dark green solution; but otherwise the reactions were the same.

Freshly prepared solutions with $x = 1$ and 2 were evaporated to dryness and the solid product was dissolved in nujol. The i.r. spectra of these solutions contained absorption peaks in the region 1150 to 850 cm^{-1}, namely at 1105, 1097, 1060, 1043 and 890 cm^{-1}, assigned as above to the alkoxide. Besides these peaks, there was a broad band in the region 700 to 400 cm^{-1} with different shape for $x = 1$ and 2. A comparison of these i.r. spectra with the one of $Sb(OEt)_3$ indicates that the green solution contains a complex of the composition close to $FeSb(OEt)_5$. The i.r. spectra of the green solution exhibited peaks at 660, 615, 513 and 434 cm^{-1}. The $FeSb(OEt)_5$ complex is expected to give absorption peaks outside the wavelength range of the u.v.–VIS spectrometer used, and accordingly the u.v.–VIS spectrum did not contain any peaks.

3.3.1. Formation and characterization of the Fe–Sb gel

The gelling of the green solution, prepared according to route 2 with $x = 2$, was accomplished by exposing it to a humidified nitrogen atmosphere. A yellow to brown X-ray amorphous powder was formed. SEM studies showed that the powder consisted of agglomerates of particles. The sizes of these particles ranged from 100 to 250 nm. Element analysis indicated that the overall Fe:Sb ratio was close to 1:2. The i.r. spectrum showed that the hydrolysis of the alkoxides was almost complete and that the gel contained only minor amounts of ethanol and H_2O. The i.r. spectrum also contained a broad peak in the Fe–O and Sb–O band region with a maximum at 604 cm^{-1} and shoulders at 740 and 500 cm^{-1}. The peak at 604 cm^{-1} probably originated from amorphous antimony oxide or hydroxide (see above). Gels used for the thermal decomposition in air were prepared by exposing the green solution to air. The yellow X-ray amorphous gel thus formed consisted of agglomerates of 75–150 nm particles, according to the SEM studies. According to the i.r. spectrum the gel contained only small amounts of solvents and H_2O, and it exhibited a broad peak in the Fe–O and Sb–O band region with a maximum at 604 cm^{-1}.

3.3.2. Thermal decomposition of the Fe–Sb gel, and characterization of the compounds formed

In connection with the studies of the decomposition of the gel in nitrogen atmosphere, a piece of the gel was transferred as fast as possible into the TG unit in order to prevent oxidation. However, it is believed that in spite of this precaution some Fe^{2+} was oxidized to Fe^{3+}. The weight loss against temperature graph of the decomposition of the gel in nitrogen is given in Fig. 3. The observed weight loss up to approximately 150 °C is most probably due to loss of excess water and ethanol (see above). The weight loss between 150 and 300 °C agrees fairly well with a transformation of $FeSb_2(OH)_8$ to $FeSb_2O_4$. The X-ray powder pattern of material quenched from 380 °C does, however, not agree with that of $FeSb_2O_4$ [8]. This is not too surprising, though, taking into account that both di- and tri-valent ion ought to be present in the material. At elevated temperatures this material starts to decompose, accompanied by sublimation of Sb_2O_3. At 950 °C the residue consists of Fe_3O_4, according to the X-ray analysis.

The thermogram of the gel prepared and heat-treated in air is given in Fig. 2. The weight loss occurring up to 180 °C is presumably associated with the loss of water and ethanol. The small weight increase observed in the temperature range 350 to 750 °C is most probably due to oxidation of the remaining Fe^{2+} to Fe^{3+}. The X-ray powder pattern of a material quenched from 950 °C shows it to be $FeSb_2O_6$ [9]. SEM studies of the material showed it to be composed of aggregates of 50–200-nm particles. The i.r. spectrum of the same material heat-treated for longer periods at elevated temperatures contained the following absorption peaks: 725, 691, 652, 566, 551 and 534 cm^{-1}.

3.4. Formation and characterization of the Co–Sb alkoxide complex

As mentioned above, the Co–Sb alkoxide complex could not be prepared by preparation routes 1 and 2. However, in an acetonitrile:toluene solution (see above), and in the presence of $Sb(OEt)_3$, $Co(OEt)_2$ dissolved easily and a wine-coloured solution was formed. In this connection it can be noted that Co ethoxide is not soluble in pure CH_3CN. Sb ethoxide is, however, easily mixed with CH_3CN. Thus when the solvent is evaporated, $Co(OEt)_2$ precipitates and liquid $Sb(OEt)_3$ remains. Upon addition of CH_3CN, the precipitate is again dissolved. The i.r. spectra discussed below have therefore been recorded in a nujol solution containing a small amount of CH_3CN in order to prevent precipitation of $Co(OEt)_2$. The i.r.

spectra of solutions with different x values showed that the complex formed probably has a composition close to $CoSb(OEt)_5$, and the spectrum of this complex exhibited peaks assigned to the ethoxide groups at 1107, 1095, 1059, 1036 and 894 cm^{-1}. In the low-energy-region peaks associated with metal–oxygen bonds could be found at 631 and 527 cm^{-1}. The u.v.–VIS spectra contained absorption peaks at 27.5, 20.5, 18.1, and a very small one at approximately 13 kK. The peak at 27.5 kK appears as a shoulder on the charge transfer component of the spectrum.

3.4.1. *Formation and characterization of the Co–Sb gel*

A lilac-coloured X-ray amorphous gel was formed by hydrolysis of a Co–Sb ethoxide solution with $x = 2$. The SEM studies showed that the gel consisted of agglomerates of particles. The sizes of the particles varied between 150 and 300 nm. Element analysis showed the overall Co:Sb ratio to be close to 1:2. The i.r. spectrum contained a broad peak in the low energy range, with a maximum at 604 cm^{-1}, originating from Sb–O bonds (see above), and shoulders at 723 and 477 cm^{-1}. The i.r. spectrum also suggested that the gel contained H_2O, CH_3CN and a minor amount of ethanol.

3.4.2. *Thermal decomposition of the Co–Sb gel, and characterization of the compounds formed*

Heating the Co–Sb gel in a nitrogen atmosphere, we observe an almost continuous weight loss up to 500 °C (see Fig. 3). This weight loss arises from evaporation of excess solvent and H_2O. The X-ray powder pattern of material quenched from 400 °C shows Sb_2O_3 to be present, and to a smaller extent $CoSb_2O_4$. The i.r. spectrum from corresponding material indicates, however, that more $CoSb_2O_4$ is present than Sb_2O_3. This indicates that the former compound largely exists in an X-ray amorphous state. The X-ray analysis of material quenched from 650 °C showed it to consist mainly of $CoSb_2O_4$. The i.r. spectrum of the same material exhibited peaks at 705, 638 and 500 cm^{-1}. According to both the i.r. spectrum and the X-ray powder diffractogram, this material does not contain any Sb_2O_3. The weight loss above 500 °C thus seems to be associated with sublimation of Sb_2O_3. At 950 °C the main residual was found to be CoO.

The weight loss against temperature curve for gel heat-treated in air is given in Fig. 2. A weight loss is observed up to approximately 350 °C after an oxidation process takes place in the temperature region 450 to 650 °C. Between 650 and 950 °C, a plateau is observed. The material quenched from 450 °C was found to be essentially X-ray amorphous (the diffractogram contained only a few unidentified weak reflections). The i.r. spectrum contained peaks resembling those of $CoSb_2O_4$ (see above). The final product formed at 950 °C consisted of $CoSb_2O_6$ [11].

3.5. Formation and characterization of the Ni–Sb alkoxide complex

Applying preparation route 1, yellow solutions were formed for $x = 0.5$, 1 and 2. Upon evaporation, yellow crystals are formed in most cases, but sometimes green crystals appear. The i.r. spectrum of the latter differs from that of the yellow ones. Element analysis of the green crystals indicated that the Ni:Sb ratio was close to 1:1, while the yellow ones exhibited a higher Ni content. Single crystal structure investigation, presently in progress, indicated that the yellow crystals had a Ni:Sb ratio of 5:3. Thus it seems that more than one type of complex is formed upon evaporation of the yellow solution. To what extent the solution contains the 5:3 ratio; or a complex with a composition close to 1:1; or both, is not known. However, the appearance of the i.r. spectra of solutions formed for $x = 0.5$, 1 and 2 suggests that the complex in the solution might have a composition close to 1:1 (see also below). The i.r. spectrum of the yellow complex exhibited peaks associated with the ethoxide groups as above, and a band at lower energies, i.e. between 400 and 650 cm^{-1}, with peaks at 605, 594, 535, and 490 cm^{-1}. The u.v.–VIS spectrum contained peaks located at 23.8 and 13.4 kK. If octahedral symmetry is assumed for the same reason as above, these peaks can be assigned to the following transitions: (i) that at 23.8 with $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$; (ii) that at 13.4 with $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$. The peaks for the Ni–Sb complex are positioned at somewhat lower energies than those of octahedral complexes such as $Ni(OEt)_2$, $NiAl_2(OEt)_8$, and $NiNb_2(OEt)_{12}$ [12–14], implying that the ligand field in the Ni–Sb complex is weaker than in the others.

3.5.1. *Formation and characterization of the Ni–Sb gel*

The yellow solution with $x = 2$ was gelled by exposing it to air. The gel consisted of transparent, green X-ray-amorphous pieces which, according to the SEM, consisted of agglomerated particles of the sizes 200–250 nm. The i.r. spectrum showed peaks associated with ethanol and water, and a strong peak at 599 cm^{-1} with a shoulder at 688 cm^{-1}, originating from metal–oxygen bonds.

3.5.2. *Thermal decomposition of the Ni–Sb gel, and characterization of the compounds formed*

The weight loss against temperature curve for the Ni–Sb gel in nitrogen is given in Fig. 3. Up to 280 °C the excess ethanol and water are evaporated. Material quenched from 400 °C consisted of $NiSb_2O_4$ according to the X-ray analysis [15]. The i.r. spectrum of this material showed peaks at 708, 646 and 506 cm^{-1}, which is in agreement with previous findings for $NiSb_2O_4$ [16]. The X-ray powder pattern of material quenched from 800 °C could be ascribed to $NiSb_2O_4$, and so could the i.r. spectrum. This implies that the weight loss between 400 °C and 800 °C (at this temperature) ought to be associated with decomposition of $NiSb_2O_4$ and sublimation of Sb_2O_3. Accordingly, NiO ought to be formed, but we have not been able to confirm this either by X-ray or by i.r. studies. At 950 °C, however, the material consisted of NiO and small amounts of Sb_2O_3.

When the gel is heat-treated in air, we observe a weight loss of approximately 10 wt % up to 400 °C associated with the loss of ethanol and water. The i.r. spectrum of material quenched from this temperature showed peaks which could be associated with those of $NiSb_2O_4$ (see above). The X-ray powder pattern contained only very weak and rather diffuse lines that could not be uniquely ascribed to $NiSb_2O_4$. Above 400 °C, the material is oxidized and $NiSb_2O_6$ is formed. This material consisted of agglomerated particles of the size 100–250 nm.

4. Conclusions

It has been shown that Cr^{2+}, Cu^{2+} and Zn^{2+} do not form any ethoxide complex of a composition close to 1:1 with Sb^{3+}, but that Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} most probably do. The properties of the latter complexes differ, however; thus the M–Sb complexes with M = Mn and Fe are very easily oxidized, the Fe–Sb complex decomposes within a few hours, the Co–Sb complex can only be formed in the presence of acetonitrile, and the Ni–Sb system is the only system where more than one type of complex seems to be formed. In this connection, it should be noted that crystal structure analysis of single crystals of the Mn complex and the Ni complex (the yellow modification) which are presently conducted show that in the solid state the Mn complex has a Mn/Sb ratio of 2:1 and the Ni complex a Ni/Sb ratio of 5:3. However, all the experimental evidence presented above seems to indicate that the various alkoxide solutions contain only one type of complex, and that this complex has a M:Sb ratio close to 1:1. Due to the metastable nature of the Fe–Sb complex, we have not been able to prepare any crystals in this system, and it seems impossible to prepare crystals of the Co–Sb complex as, upon evaporation of the acetonitrile, the complex decomposes to $Sb(OEt)_3$ and $Co(OEt)_2$.

On hydrolysis of solutions containing M and Sb species in the ratio 1:2, X-ray amorphous gels are formed for M = Mn, Fe, Co and Ni. The i.r. spectra show that the complexes have been completely hydrolysed. These gels consist of agglomerated particles ranging in size from 75 to 300 nm. Due to their small sizes it has not been possible to carry out element analysis of the individual particles, but area analyses of different parts of the agglomerates indicated that the M and Sb ions were evenly distributed.

Upon heat treatment in nitrogen atmosphere of the M–Sb gels, water and solvent are first evaporated, whereupon crystalline and/or X-ray amorphous MSb_2O_4 with M = Mn, Co and Ni is formed. The obtained lattice parameters and characteristic i.r. data for the various MSb_2O_4 oxides are given in Table I. Due to the metastable nature of the iron complex, $FeSb_2O_4$ does not seem to form, but instead as other phase forms, most probably containing Fe^{2+} as well as Fe^{3+} ions. On further heating the oxides decompose and Sb_2O_3 sublimates. The final products are NiO, CoO and Fe_3O_4, but in the case of Mn we have not so far been able to identify the end products.

Heat treatment in air of the M–Sb gels yielded MSb_2O_6 as the end product. The obtained lattice parameters and characteristic i.r. data for the various MSb_2O_6 oxides are given in Table I. In the case of Mn, several intermediate phases were formed, some of which are of unknown composition and structure. Characterization of these phases is in progress. It can also be noted that the particle sizes of the formed

TABLE I. i.r. and X-ray data of observed phases

Compound	Peaks in i.r. spectra (cm^{-1})	Lattice parameters		Reference
		a (nm)	*c* (nm)	
$MnSb_2O_4$	695, 651, 582, 499	0.87082 (5)	0.59960 (5)	This work
	680, 647, 569, 495	0.87089 (2)	0.59958 (2)	[16, 6]
$CoSb_2O_4$	705, 645, 505	0.8519 (3)	0.5932 (2)	This work
		0.849	0.591	[10]
$NiSb_2O_4$	710, 646, 605, 510	0.8408 (1)	0.5903 (9)	This work
	718, 647, 620, 520	0.8372	0.5907	[16, 15]
$MnSb_2O_6$	751, 717, 689, 633	0.8811 (1)	0.4725 (1)	This work
	608, 565, 530, 482	0.8805 (6)	0.4723 (2)	[7]
	433, 425			
$FeSb_2O_6$	725, 691, 651, 567	0.4623 (1)	0.9173 (5)	This work
	551, 534	0.463	0.914	[9]
$CoSb_2O_6$	797, 715, 688, 629	0.4652 (1)	0.9286 (1)	This work
	579, 542, 504			
	799, 700, 688, 625	0.46539	0.9283	[18, 11]
	579, 535, 502			
$NiSb_2O_6$	799, 715, 686, 634	0.46400 (1)	0.9178 (2)	This work
	595, 550, 511			
	800, 710, 635, 600	0.46415 (4)	0.9223 (3)	[18, 17]
	535, 512			

MSb_2O_6 phases were of the same order of magnitude as those found for the gels. This implies that the applied sol–gel process yields submicrometre particles of the end products.

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References

1. US Patent 2 839 554, (1958).
2. M. H. ABRAHAM, *J. Chem. Soc.* (1960) 4130.
3. C. H. BRUBAKER Jr. and M. WICHOLAS, *J. Inorg. Nucl. Chem.* **27** (1965) 59.
4. G. E. BINDER, U. ENSINGER, W. DORSCH and A. SCHMIDT, *Z. Anorg. Chem.* **507** (1983) 163.
5. B. HORVATH, R. MÖSLER and E. G. HORVATH, *Z. Anorg. Allg. Chem.* **449** (1979) 41.
6. J. R. GAVARRI, G. CALVARIN and B. CHADRON, *J. Solid State Chem.* **47** (1983) 132.
7. X. M. TURRILAS, H. VINCENT and I. RASINES, *Rev. Chem. Min.* **22** (1985) 625.
8. D. SMITH, JCPDS Grant in Aid Report JCPDS-PDS-2, 25-1181 (1973).
9. MASON and VIALIANO, *Min. Mag.* **30** (1953) 108.
10. S. STÅL, *Arkiv Kemimin. Geol.* **17B** (1943) 1.
11. National Bureau of Standards Monograph No. 25 (NBS, 1967) p. 26.
12. B. P. BARANWAL and R. C. MEHROTRA, *Aust. J. Chem.* **33** (1980) 37.
13. R. C. MEHROTRA and J. SINGH, *Can. J. Chem.* **62** (1984) 1003.
14. R. JAIN, A. K. RAI and R. C. MEHROTRA, *Z. Naturforsch.* **40B** (1985) 1371.
15. J. R. GAVARRI and A. W. HEWAT, *J. Solid State Chem.* **49** (1983) 14.
16. R. CHATER, J. R. GAVARRI and F. GENET, *ibid.* **63** (1986) 295.
17. F. LARSON and G. McCARTHY, JCPDS Grant in Aid Report JCPDS-PDS-2, 38-1083 (1986).
18. E. HUSSON, Y. REPELIN, H. BRUSSET and A. CEREZ, *Spectrochem. Acta* **35A** (1979) 1177.

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