KINETIC AND THERMODYNAMIC STABILITY OF CLUSTER COMPOUNDS UNDER HEATING

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Dehydration processes of series of rhenium cluster compounds were studied (by thermogravimetry, differential scanning calorimetry, dilatometry methods). Cluster anions of compounds are $[Re_6S_8Br_6]^{3-}$, $[Re_6S_7Br_7]^{3-}$, $[Re_6S_8(OH)_6]^{4-}$, $[Re_6Se_8(OH)_6]^{4-}$. TG- and DSC-data were used for kinetic studies, these data were processed using special computer program with 'model-free' approach. Quantitative data on thermodynamic and kinetic stability of compounds are obtained. The role of water molecules in the cluster compounds stability is discussed.

Keywords: cluster compounds, compounds stability, dehydration processes, 'model-free' kinetics

Introduction

The synthesis of chemical compounds and their existence at room temperature and atmospheric pressure are possible in principle if these compounds are thermodynamically and (or) kinetically stable in these conditions. The study of compounds transformation under heating allows to evaluate quantitatively this stability and to connect it with peculiar properties of compounds [1, 2]. For cluster compounds (synthesized from water solutions) the essential problems are the stability of the cluster ion itself, appropriate ligands selection, but also the obligatory insertion of water molecules for the formation of stable structures.
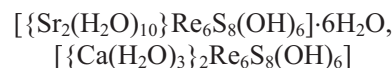
Coordination cluster compounds are usually synthesized in small-scale quantity, most of them are non-soluble in water; it is difficult to obtain their dissociation constants or reaction constants in solution (traditional quantitative characterization for coordination compounds). From this point of view the thermo-analytical investigation may give quite interesting quantitative data on kinetic and thermodynamic stability of these compounds in dehydration: reactions, deeply affected compound structure.

We studied rhenium cluster compounds. Coordination polymer compounds based on rhenium chalcohalide and chalcogenide clusters are known for a long time [3, 4]. Molecular octahedral rhenium cluster complexes with general complex anions $[Re_6Q_8L_6]$ (where Q=S, Se, Te and L=appropriate terminal ligand) were synthesized quite recently [5, 6].

Experimental

All compounds were produced by simple synthetic methods, part of them – in molten KOH, [5, 6].

Studied cluster compounds with coordinated and uncoordinated water molecules are:

$$Cs_3[Re_6S_7Br_7]\cdot H_2O, \quad Cs_4[Re_6S_8Br_6]\cdot 2H_2O$$

$$K_4[Re_6S_8(OH)_6]\cdot 8H_2O, \quad K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$$

$$[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6]\cdot 6H_2O,$$
$$[\{Ca(H_2O)_3\}_2Re_6S_8(OH)_6]$$

Detailed structures of compounds are known [5, 6].

Used thermoanalytical methods are: thermogravimetry with linear heating, differential scanning calorimetry, thermomechanic analysis (dilatometry).

Equipments: TG-209, DSC-204, TMA 202 (Netzsch), DSC-822e/700 (Mettler).

Samples masses 7–33 mg, argon flow: 20–100 cm^3 min^{-1}.

TG and DSC data were processed using the computer program 'Netzsch Thermokinetics' (version 2001.9d) [7–13]. Special program module 'model-free' allows processing several curves, obtained with different heating rates, without the information about the kinetic topochemical equations. Two different programs were used: 'Ozawa–Flynn–Wall analysis' (utilizing the dependence lg(heating rate) *vs.* $1/T$) and 'Friedman analysis' (utilizing the dependence lgdα/dt *vs.* $1/T$). They allow calculating only the activation energies for the every experimental point of fractional conversion (in the interval $0.02 < \alpha < 0.98$), so it is possible to catch sight of

stepwise passing of reaction. The same set of experimental data is used further for searching the topochemical equation (the selection from 16 equations, chemical reaction on the interface, nucleation, and diffusion). This calculation is made by the improved differential method of Borchardt–Daniels with multiple linear regression. F-test is used for the search of the best kinetic description. If the calculation results in two or three kinetics equations with near values of correlation coefficients (and F-test), but with noticeably different values of kinetics parameters, it is rationally to choose the equation with parameters values near to data of 'model-free' module programs. The application of the non-linear regression for stepwise processes was useful in some cases.

Results and discussion

$$Cs_3[Re_6S_7Br_7]\cdot H_2O \rightarrow Cs_3[Re_6S_7Br_7] + H_2O\uparrow$$
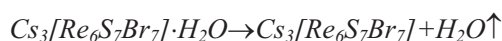
The dehydration proceeds at 40–210°C, the heating of the anhydrous compound denotes the phase transformation existence (Fig. 1). The process has two steps (Fig. 2).
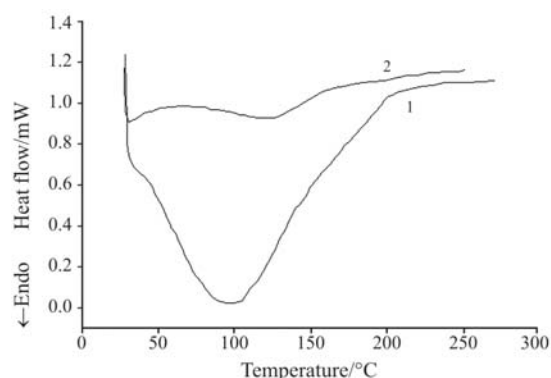

Fig. 1 DSC curves for $Cs_3[Re_6S_7Br_7]\cdot H_2O$ dehydration: for the initial compound (1) and for the anhydrous one (baseline-2). The aluminum sample holder with holes, m=14.2 mg, 10°C min^{-1}, argon flow 30 cm^3 min^{-1}. The phase transition in anhydrous compound reproduces during the repeated heating of anhydrous compound
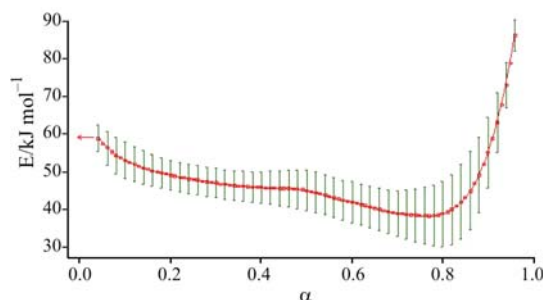

Fig. 2 Friedman analysis for $Cs_3[Re_6S_7Br_7]\cdot H_2O$ dehydration: the activation energies depending on the conversion degree. Perpendicular lines – standard deviation of calculation

Activation energy E=45–51 kJ mol^{-1} (for conversion degree α=15–50%). Linear regression gives two equations: CnB and Fn with the same correlation coefficients (0.9993) and F-test.

The non-linear regression (for consecutive reactions) gives kinetic parameters for two-step dehydration process (α=0.1–99.9%, correlation coefficient=0.999252):

- n^{th} order reaction with autocatalysis (E=47 kJ mol^{-1}, lg$A$=4.4)
- n^{th} order reaction (E_2=63 kJ mol^{-1}, lg$A$=8.1)

Graphic representation of the curve fitting is shown in Fig. 3.

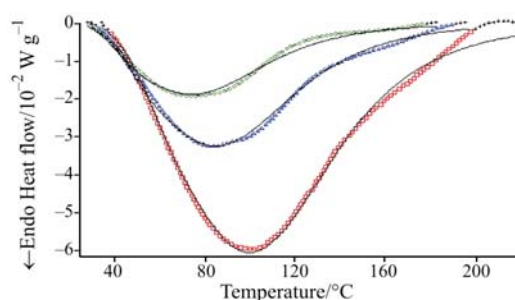**Fig. 3** Data processing for $Cs_3[Re_6S_7Br_7]\cdot H_2O$ dehydration. Curves fitting of non-linear regression, simulated with CnB (the first step) and Fn (the second step). Experimental points, calculated lines

The heat of overall dehydration reaction: Q=71 kJ mol^{-1}.

The reversible phase transition under heating proceeds at 40–180°C, 'model-free' approach gives the activation energy E=52–89 kJ mol^{-1} (within the conversion degree α=10–60%, Fig. 4). The linear regression indicates the Praut–Tompkins equation (nucleation with catalysis by reaction products): α=10–60%, E=67 kJ mol^{-1}, lg$A$=6.8 (correlation coefficient=0.945); the attempt to use the non-linear regression (for two-step reaction) is unsuccessful so as results in very big E and A values.

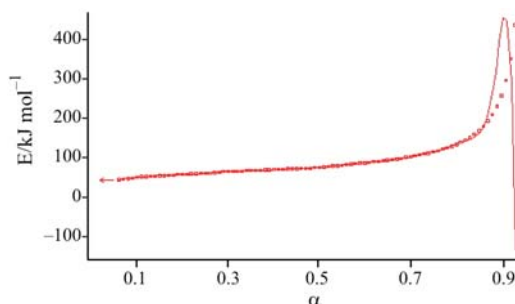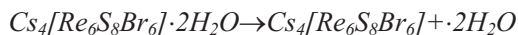The heat of this reversible phase transition: Q=5.1 kJ mol^{-1}.

Fig. 4 Friedman analysis for $Cs_3[Re_6S_7Br_7]$ phase transformation of anhydrous compound: the activation energies depending on the conversion degree

$Cs_4[Re_6S_8Br_6] \cdot 2H_2O \rightarrow Cs_4[Re_6S_8Br_6] + \cdot 2H_2O$

The dehydration proceeds at 60–130°C, the heating of the anhydrous compound denotes the phase transformation existence (Fig. 5). Experimental data were processed as above.
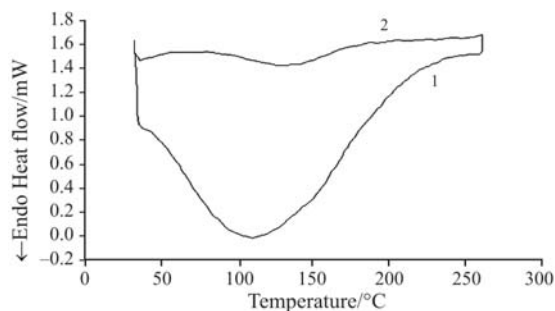

Fig. 5 DSC curves for $Cs_4[Re_6S_8Br_6] \cdot 2H_2O$ dehydration: for the initial compound (1) and for the anhydrous one (baseline-2). The aluminum sample holder with holes, m=15.3 mg, 10°C min^{-1}, argon flow 30 cm^3 min^{-1}. The phase transition in anhydrous compound reproduces during the repeated heating of anhydrous compound

The dehydration is stepwise (Fig. 6); the first dehydration step: equation of nucleation with catalysis by reaction products, α=14–46%, E=58 kJ mol^{-1}, lg$A$=5.9. The heat of overall dehydration reaction: Q=119 kJ mol^{-1}.

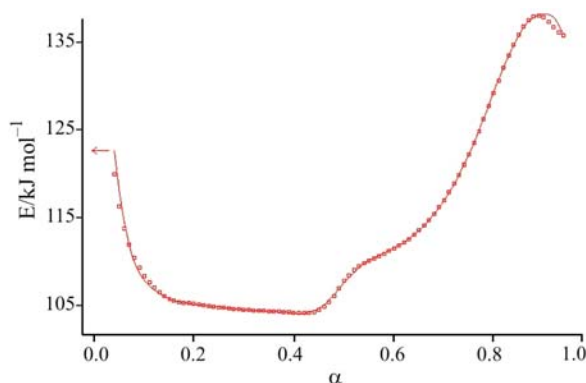**Fig. 6** Friedman analysis for $Cs_4[Re_6S_8Br_6] \cdot 2H_2O$ dehydration: the activation energies depending on the conversion degree

So as the endothermic process (without mass loss) repeats under heating of the anhydrous compound, the dehydration process is accompanied by the phase transition; calculated activation energy $E \approx 20$ kJ mol^{-1}, the heat of the phase transition $Q \approx 10$ kJ mol^{-1}.

$K_4[Re_6S_8(OH)_6] \cdot 8H_2O \rightarrow K_4[Re_6S_8(OH)_6] + 8H_2O$
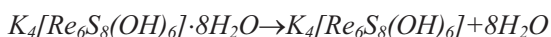
The dehydration proceeds at 20–210°C, hydroxogroups are quite stable inside the cluster anion. Dehydration is multi-step process (Fig. 7). The application
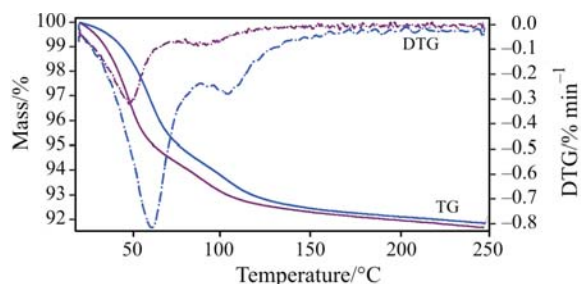

Fig. 7 TG and DTG curves for $K_4[Re_6S_8(OH)_6] \cdot 8H_2O$ dehydration; standard sample holder, heating rates 2 and 6°C min^{-1}, argon flow 30 cm^3 min^{-1}
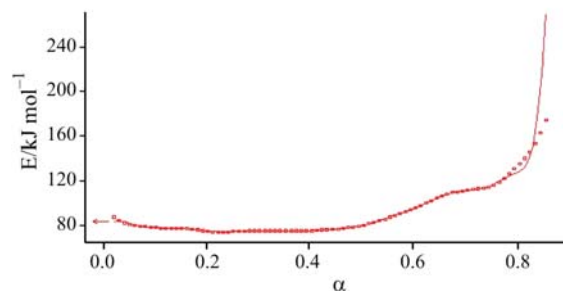

Fig. 8 Friedman analysis for $K_4[Re_6S_8(OH)_6] \cdot 8H_2O$ dehydration: the activation energies depending on the conversion degree
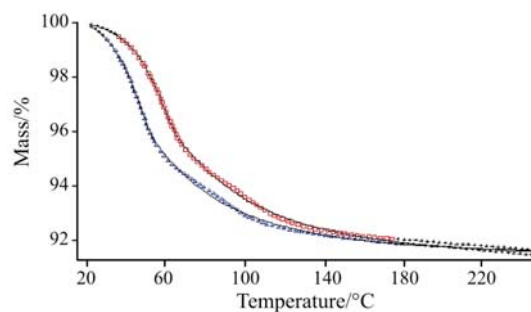
Fig. 9 Data processing for $K_4[Re_6S_8(OH)_6] \cdot 8H_2O$ dehydration. TG curves (2 and 6°C min^{-1}) fitting of non-linear regression, simulated with Fn (the first step) and Fn (the second step). Experimental points, calculated lines

of 'model-free' method (Fig. 8), linear regression method (the search of the first step kinetic parameters) and the nonlinear regression method (Fig. 9) for the all process description gave such results:

'Model-free' approach: α=5–50%, E=75–80 kJ mol^{-1}

• $K_4[Re_6S_8(OH)_6] \cdot 8H_2O \rightarrow$
  $K_4[Re_6S_8(OH)_6] \cdot 2H_2O + 6H_2O\uparrow$
  The equation: $f_1(\alpha)=(1-\alpha)^{4.3}$, E_1=70 kJ mol^{-1}, lgA_1=9.0.

• $K_4[Re_6S_8(OH)_6] \cdot 2H_2O \rightarrow$
  $K_4[Re_6S_8(OH)_6] + 2H_2O\uparrow$
  The equation: $f_2(\alpha)=(1-\alpha)^{0.4}$, E_2=71 kJ mol^{-1}, lgA_2=8.8.

$K_4[Re_6Se_8(OH)_6]\cdot 8H_2O \rightarrow K_4[Re_6Se_8(OH)_6] + 8H_2O$
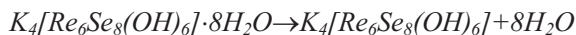
$K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ dehydrates in several steps (Figs 10 and 11), and the anhydrous cluster $K_4[Re_6Se_8(OH)_6]$ is stable up at least to 260°C. There is no phase transformation in the anhydrous compound (Fig. 11). The expressiveness of the steps is more noticeable on DSC curves (Fig. 11), although the activation energies depending on the conversion degree is very simple ($E=74\pm 3$ kJ mol^{-1} at the interval $\alpha=20$–85%, Fig. 12).
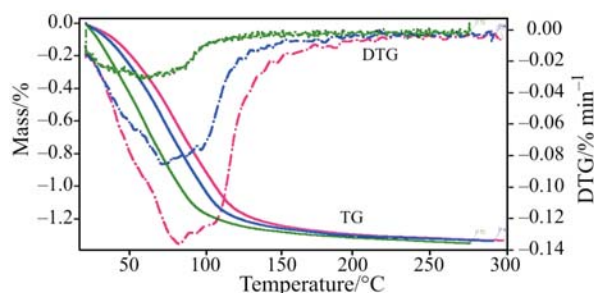

Fig. 10 TG and DTG curves for $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ dehydration; standard sample holder, heating rates 4, 8 and 12°C min^{-1}, argon flow 30 cm^3 min^{-1}
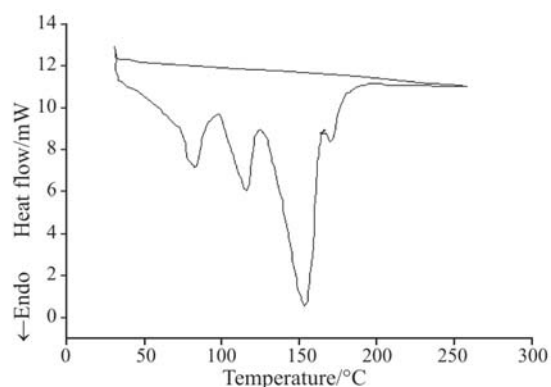

Fig. 11 DSC curves for dehydration: for $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ dehydration (with baseline). The aluminum sample holder with holes, $m=12.45$ mg, 10°C min^{-1}, argon flow 30 cm^3 min^{-1}
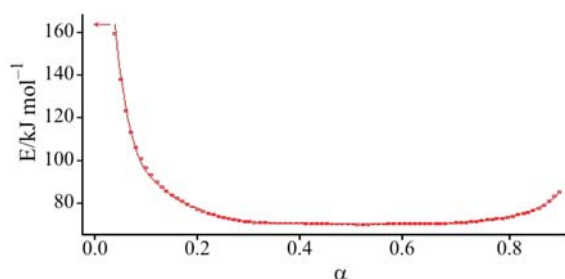

Fig. 12 Friedman analysis for $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ dehydration: the activation energies depending on the conversion degree
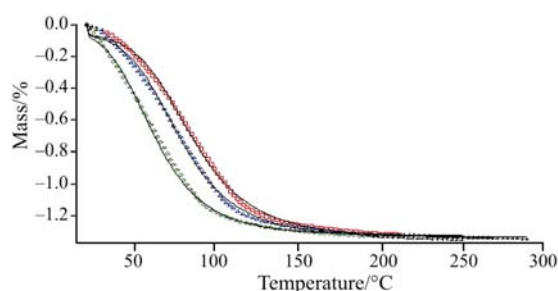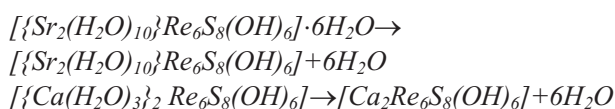

Fig. 13 Data processing for $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ dehydration. TG curves (4, 8 and 12°C min^{-1}) fitting of non-linear regression, simulated with Fn (the first step) and Fn (the second step). Experimental points, calculated lines

It turned out that the two-step reaction is quite enough for the formal kinetic description (Fig. 13).

The first dehydration step: the equation: $f_1(\alpha)=(1-\alpha)^{4.1}$, $E_1=42$ kJ mol^{-1}, lg$A_1=12.1$.

The second dehydration step: the equation: $f_2(\alpha)=(1-\alpha)^{2.5}$, $E_2=65$ kJ mol^{-1}, lg$A_2=7.5$.

The heat of overall dehydration reaction (Fig. 11): $Q=435$ kJ mol^{-1}.

$[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6]\cdot 6H_2O \rightarrow$
$[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6] + 6H_2O$
$[\{Ca(H_2O)_3\}_2 Re_6S_8(OH)_6] \rightarrow [Ca_2Re_6S_8(OH)_6] + 6H_2O$

Clusters of Sr and Ca have different structures: Sr-cluster has one-dimensional chain-like structure, Ca-cluster has two-dimensional layered structure.

$[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6]\cdot 6H_2O$ (cluster compound with both coordination water molecules, and uncoordinated ones) loses only uncoordinated water molecules, and the obtained phase is stable till 250°C at least (Fig. 14). The step curve of the dehydration process is similar to the potassium compounds (Figs 7 and 10).

$[\{Ca(H_2O)_3\}_2Re_6S_8(OH)_6]$ (cluster compound with water molecules, coordinated by Ca^{2+}-cation) loses this water molecules in one-step reaction, and the obtained phase is stable till 250°C at least (Fig. 15).
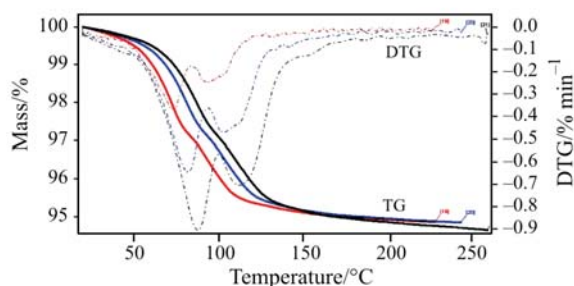

Fig. 14 TG and DTG curves for $[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6]\cdot 6H_2O$ dehydration; standard sample holder, heating rates 4, 8 and 12°C min^{-1}, argon flow 30 cm^3 min^{-1}
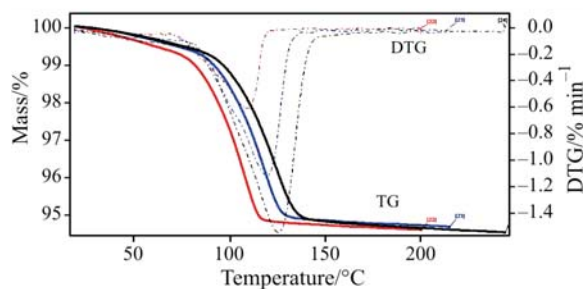
Fig. 15 TG and DTG curves for $[\{Ca(H_2O)_3\}_2 Re_6S_8(OH)_6]$ dehydration; standard sample holder, heating rates 4, 8 and 12°C min^{-1}, argon flow 30 cm^3 min^{-1}

Conclusions

Chemists often expect the very direct dependence of the dehydration process course (such as dehydration steps) upon the structure of the compound coordination sphere. As a matter of fact, dehydration steps appearance is determined in most cases by the thermodynamic stability of the possible intermediates (low-level of water) structure, the entropy factor being the more important.

TG curves are now traditional for kinetic studies. The importance of the DSC curves for kinetic studies was confirmed in publications [14, 15] and it is obvious for this work.

The processes of dehydration for monohydrate and dihydrate cluster compounds $Cs_3[Re_6S_7Br_7]\cdot H_2O$ and $Cs_4[Re_6S_8Br_6]\cdot 2H_2O$ are multi-step ones and are accompanied by reversible phase transition; heats of overall dehydration: $Q_1=71$ kJ mol^{-1}, $Q_2=119$ kJ mol^{-1}, activation energies for the first dehydration steps: $E_1=47$ kJ mol^{-1}, $E_2=67$ kJ mol^{-1}.

Heats of phase transition for anhydrous compounds: $Q'=5$ kJ mol^{-1}, $Q''=10$ kJ mol^{-1}.

These cluster compounds are stable enough without water molecules supporting, and the anhydrous compounds (only with sulfur–bromine surroundings) have tendency to phase transition, – and we repeated heating–cooling cycles four times. Heats of dehydration are rather big, the activation energies of phase transition are big enough, but heats of phase transition themselves are small (5 and 10 kJ mol^{-1}).

So we believe that the energetic barrier for initial structures distortion is big, but the distortion itself is not large.

The processes of dehydration for cluster octahydrates: $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ are multi-step ones, the anhydrous compounds are stable at least till 300°C.
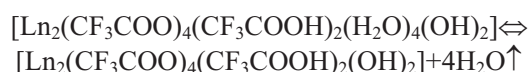
$[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6]\cdot 6H_2O$ loses only uncoordinated water molecules in the studied temperature interval, and the curve steps of the dehydration process is similar to the potassium compounds (compare Fig. 7 with Fig. 14). $[\{Ca(H_2O)_3\}_2Re_6S_8(OH)_6]$ loses the coordinated

water molecules in the same temperature interval, till 150°C (compare Fig. 14 with Fig. 15). The similar temperature interval of dehydration may be connected with different clusters structure: Sr-cluster has one-dimensional chain-like structure (coordination number of Sr is 8) and Ca-cluster has two-dimensional layered structure (coordination number of Ca is 6).

Uncoordinated water molecules more often move off in multi-step processes, coordinated ones – simultaneously; the intermediate hydrates being unstable phases (under low partial pressure of water vapor) in the first case and are quite possible in the second case.

The cluster block $[Re_6S_8(OH)_6]^{4-}$, with included hydroxyl ions, is more stable at studied temperatures than simple metal hydroxides.

Crystalline hydrates of salts of bivalent and trivalent metals (aqua–acido-complexes, in reality) often are dehydrated with high-temperature hydrolysis. The example is the dehydration of lanthanide salts of trifluoroacetic acid [16]:

$$[Ln_2(CF_3COO)_6(H_2O)_6] \Leftrightarrow$$
$$[Ln_2(CF_3COO)_4(CF_3COOH)_2(H_2O)_4(OH)_2]$$

$$[Ln_2(CF_3COO)_4(CF_3COOH)_2(H_2O)_4(OH)_2] \Leftrightarrow$$
$$[Ln_2(CF_3COO)_4(CF_3COOH)_2(OH)_2]+4H_2O\uparrow$$

Aqua–acido-coordination compounds with other acido-ligands (evidently being more strong acid) can be obtained under heating as fully anhydrous compounds: 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II); 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) [17, 18].

The rhenium cluster pack itself $[Re_6Q_8L_6]$ (where $Q=S$, Se and $L=Br^-$ and OH^- ligands) is thermodynamically and kinetically stable during dehydration reaction, minimally changing in phase transformation, and does not undergo any acid-base conversion.

Acknowledgements

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