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Synthesis and Characterisation of $TlLn(SO_4)_2 \cdot xH_2O$ (Ln = La-Tb)

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The compounds $TlLn(SO_4)_2 \cdot 2H_2O$ Ln = La, Ce, Pr, Nd and $Tl[Ln(SO_4)_2(H_2O)_3] \cdot H_2O$ Ln = Nd, Sm, Eu, Gd, Tb have been isolated from aqueous solutions of the corresponding sulfates. The dihydrates are all isomorphous and crystallize monoclinic, space group $P2_1/n$, $Z = 4$. The compounds which belong to the second type are also isomorphous and crystallize in monoclinic space group $P2_1/c$ with $Z = 4$.

The dehydration has been studied by thermogravimetry, differential scanning calorimetry and isothermal weight change determination. The dihydrates dehydrate in a single step. For the tetrahydrates the reaction is more complex, however no intermediate phases could be isolated.

The unit cell parameters, the dehydration temperatures and the dehydration enthalpies are correlated to the ionic radii of Ln^{3+}.

(Keywords: Lanthanides; Sulfates; Crystal structure; Dehydration)

Synthese und Charakterisierung von $TlLn(SO_4)_2 \cdot xH_2O$ (Ln = La-Tb)

Die Verbindungen $TlLn(SO_4)_2 \cdot 2H_2O$ Ln = La, Ce, Pr, Nd und $Tl[Ln(SO_4)_2(H_2O)_3] \cdot H_2O$ Ln = Nd, Sm, Eu, Gd, Tb wurden aus wäßrigen Lösungen der entsprechenden Sulfate isoliert. Die Dihydrate sind alle isomorph und kristallisieren monoklin, Raumgruppe $P2_1/n$, $Z = 4$. Die Verbindungen des zweiten Typs sind auch isomorph und kristallisieren in der monoklinen Raumgruppe $P2_1/c$ mit $Z = 4$.

Die Dehydration wurde mit TG, DSC und dem isothermalen Gewichtsverlust untersucht. Die Entwässerung der Dihydrate verläuft in einer Stufe, die von Tetrahydraten aber in mehreren Stufen mit keiner isolierbaren Zwischenphase.

Die Gitterkonstanten, die Dehydratations-Temperaturen und -Enthalpien wurden mit den Ionenradien von Ln^{3+} korreliert.

Introduction

There is a number of double sulfates formed by the lanthanides and univalent cations with the general formula $M^{I}Ln^{III}(SO_4)_2 \cdot xH_2O$ ($x = 4, 2, 1, 0$), which have been isolated in recent years. *Eriksson* et al.[1] prepared a series of isostructural compounds $NH_4Ln(SO_4)_2 \cdot 4\,H_2O$ and solved the crystal structure for the Sm one. According to the structure the compound should be formulated $NH_4[Ln(SO_4)_2(H_2O)_3] \cdot H_2O$. Similarly, cesium and rubidium form $M(I)[Ln(SO_4)_2(H_2O)_3] \cdot H_2O$, which are isostructural to the previous ones[2,3]. The dehydration of $Cs[Ln(SO_4)_2(H_2O)_3] \cdot H_2O$ has been studied by thermogravimetry, differential thermal analysis and isothermal weight change determination[4].

Recently $TlLa(SO_4)_2 \cdot 2\,H_2O$ has been prepared by isothermal evaporation of aqueous solution containing equivalent quantities of thallium and lanthanum sulfate and the crystal structure has been determined from single crystal data[5].

We report here the results on the synthesis, structure and thermal dehydration of the double sulfates formed between Tl_2SO_4 and $Ln_2(SO_4)_3$.

Experimental

The compounds have been prepared by isothermal evaporation at room temperature of aqueous solutions containing Tl_2SO_4 and $Ln_2(SO_4)_3$ in molar ratio 1 : 1. For Nd and Eu double sulfate eflorescence has been observed. The number of waters of crystallization has been determined by thermogravimetry.

X-ray powder analysis has been performed using a standard Philips X-ray diffractometer with $CuK\alpha_1$ radiation. The unit cell dimensions have been refined using the least-squares program SOS 2[6] with silicon ($a = 5.431065$ Å[7]) as an internal standard.

The thermoanalytical curves (TG, DSC) have been obtained by means of a Mettler Thermoanalyser TA 2000 C in a flow of dry air. Experimental conditions: sample masses 20 mg, heating rate 4 K/min, flow-rate 30 ml/min, Pt-crucibles. The DSC curves have been calibrated with the specific heat of alumina. The peak temperatures have been corrected for temperature lag.

Results and Discussion

X-ray powder data have shown two types of phases. Their unit cell parameters are given in Table 1. For Nd both phases have been isolated. On isothermal evaporation the tetrahydrate crystallizes first and then the dihydrate.

The first type $TlLn(SO_4)_2 \cdot 2\,H_2O$ (Ln = La-Nd), is isomorphous to already mentioned $TlLa(SO_4)_2 \cdot 2\,H_2O$[5]. The compounds crystallize in monoclinic space group $P2_1/n$ with $Z = 4$. The Ln atoms are nine-coordinated by O atoms in the form of a distorted monocapped square antiprism. Seven of these O atoms belong to sulfate groups and two to

Table 1. *Unit cell parameters for thallium-lanthanide sulfates*

$\mathrm{Tl}Ln(\mathrm{SO}_4)_2 \cdot 2\,\mathrm{H}_2\mathrm{O}$

Ln	*a* (Å)	*b* (Å)	*c* (Å)	(°)	*V* (Å^3)
La	7.216 (1)	11.853 (1)	10.486 (1)	92.05 (1)	896.3
Ce	7.168 (3)	11.742 (7)	10.424 (5)	92.14 (4)	876.7
Pr	7.147 (3)	11.697 (6)	10.416 (6)	92.29 (5)	870.2
Nd	7.125 (4)	11.663 (7)	10.389 (5)	92.34 (6)	862.6

$\mathrm{Tl}[Ln(\mathrm{SO}_4)_2(\mathrm{H}_2\mathrm{O})_3] \cdot \mathrm{H}_2\mathrm{O}$

Ln	*a* (Å)	*b* (Å)	*c* (Å)	(°)	*V* (Å^3)
Nd	6.600 (3)	18.913 (9)	8.719 (5)	96.23 (4)	1 081.9
Sm	6.542 (5)	18.860 (9)	8.701 (7)	96.27 (6)	1 073.5
Eu	6.525 (3)	18.841 (9)	8.694 (3)	96.27 (3)	1 062.4
Gd	6.472 (7)	18.933 (8)	8.671 (5)	96.43 (5)	1 055.8
Tb	6.490 (2)	18.782 (9)	8.642 (4)	96.71 (5)	1 046.2

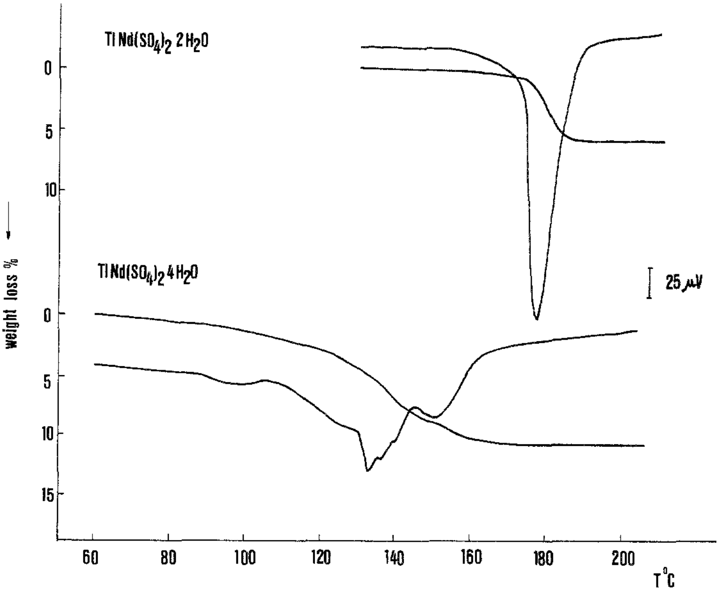

Fig. 1. TG and DSC curves of $\mathrm{TlNd(SO_4)_2 \cdot 2\,H_2O}$ and of $\mathrm{TlNd(SO_4)_2 \cdot 4\,H_2O}$

Table 2. *Experimental and calculated weight losses for the dehydration of thallium-lanthanide sulfates*

$TlLn(SO_4)_2 \cdot 2H_2O$			$Tl[Ln(SO_4)_2(H_2O)_3] \cdot H_2O$		
Ln	Δm_{exp} (%)	Δm_{cal} (%)	*Ln*	Δm_{exp} (%)	Δm_{cal} (%)
La	6.1	6.31	Nd	11.2	11.76
Ce	6.1	6.29	Sm	11.3	11.64
Pr	6.1	6.28	Eu	11.3	11.62
Nd	6.1	6.25	Gd	11.5	11.52
			Tb	11.2	11.49

Table 3. *Temperatures and enthalpies for the dehydration of thallium-lanthanide sulfates*

$TlLn(SO_4)_2 \cdot 2H_2O$

Ln	$T_{begin.}$ (°C)	DSC peak (°C)	$\Delta H_{deh.}$ (kJ/mol)
La	140	159	104(3)
Ce	145	161	105(3)
Pr	150	168	109(3)
Nd	160	175	110(3)

$Tl[Ln(SO_4)_2(H_2O)_3] \cdot H_2O$

Ln	DSC peak (°C)	$\Delta H_{deh.}$ (kJ/mol)
Nd	132	190(4)
Sm	126	192(4)
Eu	125	204 (4)
Gd	129	196 (4)
Tb	123	236 (4)

water molecules. The Tl atoms are coordinated also by nine O atoms in the form of an irregular polyhedron. Again, seven O atoms belong to sulfates and two to water molecules. The sulfate groups join *Ln* and Tl polyhedra into a three-dimensional framework.

The second type of compounds $TlLn(SO_4)_2 \cdot 4H_2O$ (*Ln* = Nd-Tb) is isomorphous to $M(I)[Ln(SO_4)_2(H_2O)_3] \cdot H_2O$ (M = Rb, Cs, NH_4)[1-3]. These double sulfates are monoclinic with space group $P2_1/c$ and $Z = 4$. The polyhedron around *Ln* is the same as in dihydrates, however six O atoms belong to sulfate groups and three to water molecules. *Ln*-

polyhedra are bound to a layer-like structure with Tl ions and with the rest of water molecules between the layers.

As shown in Table 1, the unit cell dimensions together with the unit cell volumes decrease as expected.

TG and DSC curves for the dehydration of $TlNd(SO_4)_2 \cdot 2H_2O$ and $Tl[Nd(SO_4)_2(H_2O)_3] \cdot H_2O$ are shown in Fig. 1, and the corresponding mass losses in Table 2. Characteristic temperatures together with the dehydration enthalpies are given in Table 3.

For the dihydrates the reaction is completed in one step within the temperature interval 140–200 °C. The beginning of the dehydration, the DSC peak temperatures and the enthalpies show the same trend as do the unit cell parameters. In $TlLa(SO_4)_2 \cdot 2H_2O$ the water molecule has the following bond distances: La-OH_2 2.577 (8) and 2.615 (7) Å and Tl-OH_2 3.234 (7) and 3.316 (8) Å[5]. Water molecules are therefore bound more strongly to Ln^{3+} than to Tl^{+}, which explains the dependence of the dehydration data (Table 3) on the ionic radii of Ln^{3+}.

Tetrahydrates dehydrate in the temperature range 50–200 °C, the onset of the reaction being the same for all of them. The dynamic TG curves are similar to those for cesium double sulfates[4], where a number of stable monohydrates (Pr, Nd, Sm, Eu, Gd) could be isolated isothermally. Contrary to cesium compounds, isothermal weight change determinations even at 60, 70 and 80 °C show a steady decrease in mass for thallium hydrates. X-ray powder photographs of several intermediates phases show the patterns of initial and/or dehydrated compound only. For Nd the lines of the dihydrate appear also, the phase however can not be isolated in this way. The dehydration temperatures as well as the dehydration enthalpies (Table 3) exhibit no regularity.

Acknowledgement

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