Thermochimica Acta, 123 (1988) 23–31
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS OF THE HYDRATES OF CHLORINATED ACETATES OF RARE EARTHS AND THEIR THERMAL BEHAVIOUR *

XIONG WEIMIAO

Department of Chemistry, Northwest University, Xian, Shaanxi (People's Republic of China)

WU SHURONG and MENG YAN

Thermochemical Research Laboratory, Northwest University, Xian, Shaanxi (People's Republic of China)

(Received 13 January 1987)

ABSTRACT

The dehydration processes and their enthalpy changes for the hydrates of the monochloroacetates, dichloroacetates and trichloroacetates of lanthanum, cerium, praseodymium, neodymium, samarium, europium and gadolinium have been investigated by means of TG, dehydration over P_2O_5 and DSC. The thermal decomposition mechanisms of the anhydrous dichloroacetates have also been studied by using elemental analysis, IR and DTA–TG–DTG techniques. The mechanisms revealed that the decompositions occur in two stages in the range from room temperature to 600 ° C. In the first stage the anhydrous salts decompose to form the intermediate products, $Ln_2(OH)Cl_5 \cdot 3H_2O$ ($Eu_2(OH)Cl_5 \cdot 2H_2O$ in the case of the europium salt) which then decompose further to the rare earth oxychlorides LnOCl (CeO_2 in the case of the cerium salt) in the second stage.

INTRODUCTION

In studies of the separation of the rare earth elements and of their coordination properties, attention has been focused mainly on the halogenated acetates of the rare earths. The synthesis of the monochloroacetate (I), dichloroacetate (II) and trichloroacetate (III) hydrates of lanthanum, cerium, praseodymium, neodymium, samarium, europium and gadolinium and some of their properties have been investigated by many researchers [1–9] but the number of water molecules for the same kind of hydrated salt synthesized by different researchers is not always the same. As yet, reports on the dehydration processes and enthalpies of the hydrates and

---

* Paper presented at the Sino-Japanese Joint Symposium on Calorimetry and Thermal Analysis, Hangzhou, People's Republic of China, 5–7 November 1986.

0040-6031/88/$03.50

the thermal decomposition mechanisms of the anhydrous dichloroacetates have not been found in the literature. In this paper, compounds I, II and III were synthesized and characterized by elemental analysis, TG and dehydration over P_2O_5. These hydrates, except $Nd(CH_2ClCOO)_3 \cdot 2H_2O$ and $La(CCl_3COO)_3 \cdot 3H_2O$, are new. The dehydration processes of the hydrated salts and the thermal decomposition mechanisms of the anhydrous dichloroacetates were studied by elemental analysis, IR and DTA–TG–DTG techniques; the dehydration enthalpies of the hydrates were determined by DSC.

EXPERIMENTAL

Synthesis

Compounds I were prepared as follows. An excess of a rare earth oxide was added to 50% monochloroacetic acid and the mixture was allowed to react completely at room temperature. The excess oxide was filtered off. The crystalline material in each case was obtained after storing the filtrate for several days in an evacuated (30 mm Hg) desiccator containing NaOH. The crystals were washed with absolute ethyl alcohol and ether, and then placed in the same desiccator until they reached a constant weight.

Compounds II and III were obtained using the following method. The rare earth oxide was dissolved in HCl (6 mol dm^{-3}) and $(NH_4)_2CO_3$ solution was added to the solution. An excess of the precipitate obtained, $Ln_2(CO_3)_3 \cdot XH_2O$, was allowed to react with 50% dichloroacetic or trichloroacetic acid. Any excess carbonate was filtered off and compounds II and III were then obtained from the filtrate in the same manner as described above.

Composition analysis

The rare earth elements were estimated by ethylenediaminetetracetic acid (EDTA) titration with xylenol orange as an indicator. The carbon and hydrogen were determined with an elemental analyzer (made in China). The chlorine was determined using the oxygen flask method [10] and the number of molecules of hydration water was estimated by TG.

Experimental conditions

The dehydration of compounds I, II and III and the thermal decomposition of the anhydrous dichloroacetates were carried out with an LCT differential thermobalance connected with a WF-1 differentiator (Beijing Optical Instrument Factory). The following experimental conditions were used: atmosphere, static air in an open protection tube; DTA scale, ±100

μV; TG scale, 10 mg; DTG scale, 5 mV min^{-1}; heating rate, 5 °C min^{-1}; chart speed, 4 mm min^{-1}.

The dehydration enthalpies of compounds I were measured on a CDR-1 differential scanning calorimeter (Shanghai Tienping Instrument Factory). The following experimental conditions were used: DSC scale, ± 1 mcal s^{-1}, heating rate, 5 °C min^{-1}; chart speed, 10 mm min^{-1}; atmosphere, dry nitrogen at a flow rate of 40 ml min^{-1}. The calorific capacity of DSC was calibrated using the fusion enthalpy of metadihydroxybenzene as a standard.

The measurements of the dehydration enthalpies of compounds II and III were performed on a Perkin–Elmer DSC-2C differential scanning calorimeter. The experimental conditions were the same as above. The fusion enthalpy of indium spectrograde was chosen as a calibration standard for the calorific capacity.

IR spectra of the intermediate products of the anhydrous dichloroacetates were recorded with a DS-701G spectrophotometer using a KBr pellet.

RESULTS AND DISCUSSION

The results of the composition analyses for compounds I, II and III are presented in Table 1.

In order to verify the number of molecules of water of hydration determined by TG, we arbitrarily selected the hydrates of cerium, praseodymium, neodymium, samarium, europium and gadolinium monochloroacetates, the hydrates of lanthanum, cerium and praseodymium dichloroacetates and the hydrates of cerium, praseodymium and neodymium trichloroacetates, allowed them to remain in a vacuum desiccator over P_2O_5 to constant weight and then determined the contents of the rare earths and the chlorine in the resulting substances. The results (see Table 2) are in good agreement with the calculated values.

As a typical example of the monochloroacetate hydrates, the thermal analysis curves for the dehydration of $La(CH_2ClCOO)_3 \cdot 1.5H_2O$ are shown in Fig. 1.

The thermal analysis curves for the dehydration and further decomposition of lanthanum dichloroacetate hydrate were used as typical examples of the dichloroacetate hydrates (see Fig. 2). The thermal analysis curves for the dehydration of $Ce(CCl_3COO)_3 \cdot 2H_2O$ were used as typical examples of the trichloroacetate hydrates (see Fig. 3).

In Table 3 and in Figs. 1–3, we observe that the dehydration processes of compounds I all take place in a single step; those of compounds II take place in two or three steps, except those of lanthanum, cerium and gadolinium salts which are single-step processes; the dehydration of compounds III occurs in three steps, except that of praseodymium and neodymium salts which occurs in two steps. Thus it can be seen that the dehydration

TABLE 1

Analytical data for compounds I, II and III

Hydrate	Ln (%)		Cl (%)		C (%)		H (%)		Water of hydration (mol)	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$La(CH_2ClCOO)_3 \cdot 1.5H_2O$	31.12	31.15	23.83	23.76	16.14	15.79	2.03	2.10	1.5	1.48
$Ce(CH_2ClCOO)_3 \cdot 1.5H_2O$	31.37	30.59	23.82	23.44	16.14	16.41	1.69	1.92	1.5	1.51
$Pr(CH_2ClCOO)_3 \cdot 1.5H_2O$	31.43	31.60	23.72	23.80	16.07	16.28	2.02	2.08	1.5	1.53
$Nd(CH_2ClCOO)_3 \cdot 2H_2O$	31.31	31.88	23.08	23.13	15.64	–	2.19	–	2	2.00
$Sm(CH_2ClCOO)_3 \cdot 1.5H_2O$	32.84	32.91	23.23	23.87	15.74	15.32	1.98	2.07	1.5	1.51
$Eu(CH_2ClCOO)_3 \cdot 1.5H_2O$	33.08	33.22	23.15	23.62	15.69	15.00	1.97	1.95	1.5	1.57
$Gd(CH_2ClCOO)_3 \cdot 2H_2O$	33.20	34.32	22.45	22.41	15.21	14.86	2.13	2.18	2	1.80
$La(CHCl_2COO)_3 \cdot 2H_2O$	24.86	24.90	38.07	37.71	–	–	–	–	2	1.98
$Ce(CHCl_2COO)_3 \cdot 2H_2O$	25.02	24.90	37.99	37.46	–	–	–	–	2	2.09
$Pr(CHCl_2COO)_3 \cdot 1.75H_2O$	25.33	25.32	38.24	38.14	–	–	–	–	1.75	1.76
$Nd(CHCl_2COO)_3 \cdot 2H_2O$	25.57	25.48	37.71	37.48	–	–	–	–	2	1.85
$Sm(CHCl_2COO)_3 \cdot 1.5H_2O$	26.79	26.70	37.90	37.55	–	–	–	–	1.5	1.48
$Eu(CHCl_2COO)_3 \cdot 1.25H_2O$	27.22	27.04	38.10	38.02	–	–	–	–	1.25	1.25
$Gd(CHCl_2COO)_3 \cdot H_2O$	28.12	28.38	38.04	37.57	–	–	–	–	1	0.99
$La(CCl_3COO)_3 \cdot 3H_2O$	20.42	20.48	46.92	47.28	–	–	–	–	3	2.87
$Ce(CCl_3COO)_3 \cdot 2H_2O$	21.12	21.05	48.11	47.78	–	–	–	–	2	2.01
$Pr(CCl_3COO)_3 \cdot 1.5H_2O$	21.51	21.24	48.71	48.54	–	–	–	–	1.5	1.59
$Nd(CCl_3COO)_3 \cdot 2H_2O$	21.61	20.96	47.81	46.38	–	–	–	–	2	2.06
$Sm(CCl_3COO)_3 \cdot 2H_2O$	22.32	22.20	47.37	47.11	–	–	–	–	2	1.98
$Eu(CCl_3COO)_3 \cdot 2.5H_2O$	22.21	22.47	46.64	46.86	–	–	–	–	2.5	2.60
$Gd(CCl_3COO)_3 \cdot 2H_2O$	23.11	23.00	46.89	46.60	–	–	–	–	2	2.04

TABLE 2

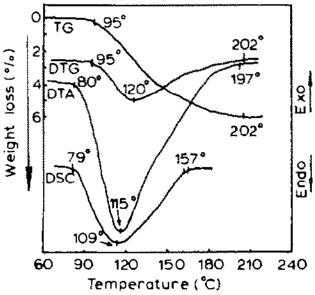
Analytical data of the anhydrous salts

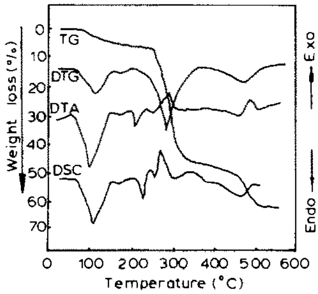
Anhydrous salt	Dehydration of hydrate (mol)		Ln (%)		Cl (%)	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$Ce(CH_2ClCOO)_3$	1.50	1.53	33.32	31.97	25.29	25.22
$Pr(CH_2ClCOO)_3$	1.50	1.50	33.44	33.28	25.24	25.20
$Nd(CH_2ClCOO)_3$	2.00	1.90	33.96	33.29	25.04	25.57
$Sm(CH_2ClCOO)_3$	1.50	1.51	34.90	34.80	24.69	24.45
$Eu(CH_2ClCOO)_3$	1.50	1.51	35.14	35.05	24.60	24.99
$Gd(CH_2ClCOO)_3$	2.00	1.87	35.92	36.52	24.30	24.01
$La(CHCl_2COO)_3$	2.00	2.00	26.57	26.70	40.70	39.98
$Ce(CHCl_2COO)_3$	2.00	2.08	26.74	26.64	40.60	39.64
$Ce(CCl_3COO)_3$	2.00	2.04	22.34	22.44	50.87	48.97
$Pr(CCl_3COO)_3$	1.50	1.53	22.44	22.28	50.80	50.53
$Nd(CCl_3COO)_3$	2.00	2.01	22.84	22.37	50.54	49.23

processes of the hydrates become more and more complex with increasing number of chlorine atoms in the chlorinated acetates.

According to the area of the DSC peak, it is easy to find the corresponding dehydration enthalpy. The dehydration processes, enthalpy changes and other related data for compounds I, II and III are all given in Table 3.

The data on the thermal analysis curves for the further decomposition of the anhydrous dichloroacetates of the rare earths are listed in Table 4. From Table 4, we can see that the thermal decomposition of the six anhydrous salts takes place in two main stages, namely, the anhydrous salts decompose and further form the intermediate products, $Ln_2(OH)Cl_5 \cdot 3H_2O$ ($Eu_2(OH)Cl_5 \cdot 2H_2O$ in the case of the europium salt), which then decom-





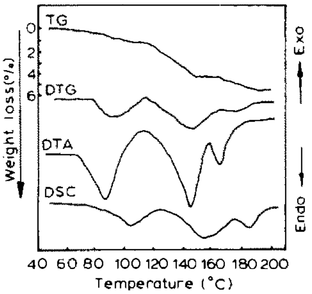


Fig. 1. Thermal analysis curves of $La(CH_2ClCOO)_3 \cdot 1.5H_2O$.

Fig. 2. Thermal analysis curves of $La(CHCl_2COO)_3 \cdot 2H_2O$.

Fig. 3. Thermal analysis curves of $Ce(CCl_3COO)_3 \cdot 2H_2O$.

TABLE 3

Dehydration stages and enthalpies for compounds I, II and III [a]

Dehydration stages	Weight loss (mg)		DSC temp. range (°C)	Dehydration enthalpy [b] (kJ (mol H_2O)$^{-1}$)
	Calc.	Obs.		
$LaL'_3\cdot 1.5H_2O \rightarrow LaL'_3$	0.81	0.80	79–109–157	65.2 ± 1.1
$CeL'_3\cdot 1.5H_2O \rightarrow CeL'_3$	0.76	0.76	73–105–148	60.1 ± 0.4
$PrL'_3\cdot 1.5H_2O \rightarrow PrL'_3$	0.91	0.93	78–114–156	68.0 ± 0.4
$NdL'_3\cdot 2H_2O \rightarrow NdL'_3$	0.96	0.96	74–144–196	47.6 ± 0.6
$SmL'_3\cdot 1.5H_2O \rightarrow SmL'_3$	0.77	0.78	70–108–124	73.1 ± 1.2
$EuL'_3\cdot 1.5H_2O \rightarrow EuL'_3$	0.84	0.88	72–102–131	63.5 ± 0.2
$GdL'_3\cdot 2H_2O \rightarrow GdL'_3$	1.10	1.00	73–105–150	49.1 ± 0.4
$LaL''_3\cdot 2H_2O \rightarrow LaL''_3$	0.77	0.76	61–109–181	42.2
$CeL''_3\cdot 2H_2O \rightarrow CeL''_3$	0.77	0.80	74–119–157	25.0
$PrL''_3\cdot 1.75H_2O \rightarrow PrL''_3\cdot H_2O$	0.31	0.31	55–86–114	48.8
$PrL''_3\cdot H_2O \rightarrow PrL''_3$	0.40	0.41	114–138–202	61.6
$NdL''_3\cdot 2H_2O \rightarrow NdL''_3\cdot H_2O$	0.39	0.37	47–105–120	40.7
$NdL''_3\cdot H_2O \rightarrow NdL''_3$	0.39	0.37	118–156–196	62.5
$SmL''_3\cdot 1.5H_2O \rightarrow SmL''\cdot 1.25H_2O$	0.10	0.10	43–61–72	93.7
$SmL''_3\cdot 1.25H_2O \rightarrow SmL''_3\cdot H_2O$	0.10	0.10	72–86–106	49.8
$SmL''_3\cdot H_2O \rightarrow SmL''_3$	0.39	0.38	112–164–190	56.2
$EuL''_3\cdot 1.25H_2O \rightarrow EuL''_3\cdot H_2O$	0.10	0.10	24–58–96	35.1
$EuL''_3\cdot H_2O \rightarrow EuL''_3$	0.40	0.40	132–174–207	69.8
$GdL''_3\cdot H_2O \rightarrow GdL''_3$	0.39	0.40	110–176–205	86.9
$LaL'''_3\cdot 3H_2O \rightarrow LaL'''_3\cdot 2.5H_2O$	0.14	0.16	33–64–75	9.1
$LaL'''_3\cdot 2.5H_2O \rightarrow LaL'''_3\cdot 2H_2O$	0.14	0.14	75–101–116	27.1
$LaL'''_3\cdot 2H_2O \rightarrow LaL'''_3$	0.58	0.53	116–162–198	38.2
$CeL'''_3\cdot 2H_2O \rightarrow CeL'''_3\cdot 1.5H_2O$	0.17	0.18	74–102–117	42.2
$CeL'''_3\cdot 1.5H_2O \rightarrow CeL'''_3\cdot 0.5H_2O$	0.35	0.35	117–172–179	52.6
$CeL'''_3\cdot 0.5H_2O \rightarrow CeL'''_3$	0.17	0.18	179–184–197	36.5
$PrL'''_3\cdot 1.5H_2O \rightarrow PrL'''_3\cdot 1.25H_2O$	0.08	0.07	74–101–120	75.0
$PrL'''_3\cdot 1.25H_2O \rightarrow PrL'''_3$	0.39	0.43	120–176–207	77.0
$NdL'''_3\cdot 2H_2O \rightarrow NdL'''_3\cdot 1.5H_2O$	0.16	0.18	50–73–115	53.8
$NdL'''_3\cdot 1.5H_2O \rightarrow NdL'''_3$	0.47	0.47	115–166–188	35.0
$SmL'''_3\cdot 2H_2O \rightarrow SmL'''_3\cdot 1.75H_2O$	0.07	0.07	84–102–118	53.9
$SmL'''_3\cdot 1.75H_2O \rightarrow SmL'''_3\cdot 0.75H_2O$	0.27	0.26	118–160–173	42.7
$SmL'''_3\cdot 0.75H_2O \rightarrow SmL'''_3$	0.20	0.20	173–202–221	55.5
$EuL'''_3\cdot 2.5H_2O \rightarrow EuL'''_3\cdot 2H_2O$	0.14	0.15	85–105–119	26.4
$EuL'''_3\cdot 2H_2O \rightarrow EuL'''_3\cdot 0.5H_2O$	0.43	0.44	119–159–174	27.0
$EuL'''_3\cdot 0.5H_2O \rightarrow EuL'''_3$	0.14	0.15	174–203–219	89.6
$GdL'''_3\cdot 2H_2O \rightarrow GdL'''_3\cdot 1.75H_2O$	0.07	0.10	81–103–117	45.3
$GdL'''_3\cdot 1.75H_2O \rightarrow GdL'''_3\cdot 0.75H_2O$	0.29	0.29	117–153–170	38.5
$GdL'''_3\cdot 0.75H_2O \rightarrow GdL'''_3$	0.22	0.20	170–204–220	54.1

[a] $L' \equiv CH_2ClCOO^-$; $L'' \equiv CHCl_2COO^-$; $L''' \equiv CCl_3COO^-$.

[b] Average of six experiments for compounds I and of three experiments for the others.

pose to the rare earth oxychlorides LnOCl (CeO_2 in the case of the cerium salt) as final products (the highest temperature used was only about 600 °C; gaseous products were not detected).

TABLE 4

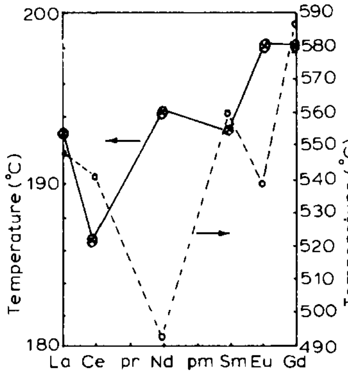
Thermal decomposition stages and their related data for the anhydrous rare earth dichloroacetates [a]

Decomposition stage	Temperature range (°C)			Weight loss (mg)	
	TG	DTG	DTA	Calc.	Obs.
$LaL_3 \rightarrow La_2(OH)Cl_5 \cdot 3H_2O$	193–343	193–245–343	199–237–372	5.58	5.63
$La_2(OH)Cl_5 \cdot 3H_2O \rightarrow LaOCl$	343–547	343–378–547	372–497–544	1.56	1.51
$CeL_3 \rightarrow Ce_2(OH)Cl_5 \cdot 3H_2O$	186–345	188–264–352	188–232–334	5.52	5.51
$Ce_2(OH)Cl_5 \cdot 3H_2O \rightarrow CeO_2$	345–542	352–421–542	344–369–505	1.97	1.91
$NdL_3 \rightarrow Nd_2(OH)Cl_5 \cdot 3H_2O$	194–343	194–261–343	195–256–376	5.60	5.66
$Nd_2(OH)Cl_5 \cdot 3H_2O \rightarrow NdOCl$	343–491	343–440–491	376–460–491	1.58	1.57
$SmL_3 \rightarrow Sm_2(OH)Cl_5 \cdot 3H_2O$	193–366	193–266–368	184–266–383	5.57	5.67
$Sm_2(OH)Cl_5 \cdot 3H_2O \rightarrow SmOCl$	380–601	380–541–601	383–558–580	1.56	1.55
$EuL_3 \rightarrow Eu_2(OH)Cl_5 \cdot 2H_2O$	198–363	198–277–363	198–258–363	5.97	6.08
$Eu_2(OH)Cl_5 \cdot 2H_2O \rightarrow EuOCl$	363–538	363–474–538	363–460–533	1.41	1.27
$GdL_3 \rightarrow Gd_2(OH)Cl_5 \cdot 3H_2O$	198–376	198–283–378	195–254–377	5.56	5.60
$Gd_2(OH)Cl_5 \cdot 3H_2O \rightarrow GdOCl$	376–587	378–587	377–472–528	1.56	1.50

[a] $L \equiv CHCl_2COO^-$.

The following experimental data confirm these conclusions.

1. The agreement between the composition analyses of the resulting substances and the calculated values for the anhydrous salts show that the anhydrous salts do indeed exist.



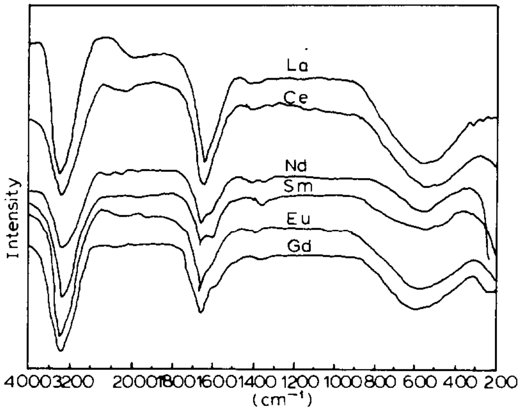


Fig. 4. IR spectra of the intermediate products of the anhydrous dichloroacetates of the rare earths (KBr pellet).

Fig. 5. The relationship between the final temperatures for forming the anhydrous salts and oxychlorides and the atomic number: ⊗, anhydrous salts; ○, oxychlorides (CeO_2 in the case of the cerium salt).

TABLE 5

Analytical data of the chlorine content in the intermediate products

Intermediate product	Chlorine (%)	
	Calc.	Obs.
$La_2(OH)Cl_5 \cdot 3H_2O$	33.69	33.29
$Ce_2(OH)Cl_5 \cdot 3H_2O$	33.54	34.04
$Nd_2(OH)Cl_5 \cdot 3H_2O$	33.02	31.23
$Sm_2(OH)Cl_5 \cdot 3H_2O$	32.29	30.52
$Eu_2(OH)Cl_5 \cdot 2H_2O$	33.18	32.98
$Gd_2(OH)Cl_5 \cdot 3H_2O$	31.50	31.63

2. The weight losses on TG curves are in good agreement with the values calculated on the basis of the assumed decomposition stages.

3. The IR spectra of the intermediate products for different rare earths are similar (see Fig. 4). In Fig. 4, it can be observed that the characteristic COO^- stretching frequencies ($\nu_{asym} \approx 1600$ cm^{-1}; $\nu_{sym} \approx 1410$ cm^{-1}) and C–halogen stretching frequencies ($\nu_{asym} \approx 830$ cm^{-1}; $\nu_{sym} \approx 730$ cm^{-1}) in the dichloroacetates almost disappear, and the characteristic absorption frequencies of the water of hydration only are exhibited [11]. These observations mean that the acetates decompose almost completely to yield the intermediate products.

4. The values of the determined chlorine content in the intermediate products are consistent with the values calculated from the assumed compositions (see Table 5).

5. The characteristic IR absorption spectra of the final products are also in good agreement with reported data [12,13].

In addition, if the final temperatures for forming the anhydrous salts and oxychlorides (from Table 4) are plotted against the atomic number of the rare earths, the double-double effects [14] of the lanthanides will be observed (see Fig. 5).

ACKNOWLEDGEMENT

The authors are very grateful to Prof. Chen Yun-Sheng for his valuable assistance.

REFERENCES

1 S.S. Krishnamurthy and S. Soundararajan, J. Less-Common Met., 16 (1968) 1.
2 J. Porkorny and F. Petru, Z. Chem., 12 (1972) 294.
3 M. Singh and S.N. Misra, Synth. React. Inorg. Met.-Org. Chem., 8 (1978) 389.

4 L.M. Vdovina and L.L. Kuznetzova, Russ. J. Inorg. Chem., 26 (1981) 1546.
5 R.C. Paul, G. Singh and J.S. Ghotra, Indian J. Chem., 11 (1973) 294.
6 M. Singh, M.P. Bhutra, P.P. Vaishnava and S.N. Misra, Bull. Chem. Soc. Jpn., 51 (1978) 1241.
7 G.P. Tilley and J.E. Roberts, Inorg. Chem., 2 (1963) 745.
8 V.N. Krishnamurthy and S. Soundararajan, J. Less-Common Met., 13 (1967) 263.
9 B.S. Mathur and T.R. Bhat, Z. Anorg. Allg. Chem., 343 (1966) 220.
10 W. Schoniger, Mikrochim. Acta, (I) (1955) 123.
11 R.J. Morrow and A. Palm, J. Inorg. Nucl. Chem., 24 (1962) 239.
12 A. Rulmont, Spectrochim. Acta, Part A, 28 (1972) 1287.
13 Sadtler, Research Laboratories, Inorganics IR Grating Spectra, Vols. 1 and 2, Sadtler Research Laboratories, Philadelphia, 1965 Y195K.
14 I. Fidelis and S. Siekierski, J. Inorg. Nucl. Chem., 28 (1966) 185; 34 (1972) 2225.