Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 143-154

SOME POLYNUCLEAR COORDINATION COMPOUNDS PRECURSORS OF CHROMITES

Synthesis, physicochemical characterization and thermal stability

V. Pocol[1], *L. Patron*[1], *O. Carp*[1*], *M. Brezeanu*[2], *E. Segal*[3], *N. Stanica*[1] *and D. Crisan*[1]

[1]Institute of Physical Chemistry, Splaiul Independentei, Nr. 202, sector 6, Bucharest
[2]Department of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest
Dumbrava Rosie Street, Nr. 23, sector 2, Bucharest
[3]Department of Physical Chemistry, Faculty of Chemistry, University Bucharest, Bulevardul Carol Republicii, Nr. 13, Bucharest, Romania

(Received March 7, 1998)

Abstract

The polynuclear coordination compounds LnCr(tartrate)$_3\cdot n$H$_2$O where *Ln*(III)=La-Er, obtained through a precipitation method, were characterized on the basis of elemental analysis, their electronic and vibrational spectra and magnetic susceptibility measurements. The possibility of obtaining chromites through the transformations of the polynuclear coordination compounds in the solid state was considered. The thermal decompositions of these compounds, studied by TG and DTA methods, were found to follow an almost uniform pattern. The decompositions occurred in six–eight steps. The first two steps involved dehydration, and the third the transformation of tartrate anions to oxalate, followed by conversion to carbonate and oxocarbonate intermediates. The final product in each case was LnCrO$_3$. A non-isothermal kinetic analysis of the first decomposition steps was performed, the most probable decomposition mechanism being selected and the kinetic parameters evaluated. The final products of the transformations were characterized.

Keywords: chromites, polynuclear coordination compounds, precursors

Introduction

The literature frequently reports the use of mixed oxides containing lanthanide and transition metals as catalysts in redox reactions [1], in hydrogenation reactions [2] and as automobile exhaust catalysts [3] with high catalytic activity.

In order to avoid the difficulties encountered in the ceramic method [4], in recent years new nonconventional methods have been developed, such as the ther-

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[*] Author to whom all correspondence should be addressed.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

mal decomposition of metal-organic and polynuclear [5] coordination [6–9] precursors.

Experimental

Synthesis

Polynuclear coordination compounds were separated from the reaction media (solutions containing Ln(III)-Cr(III)-tartaric acid) by extraction with ethanol. For complete precipitation, 24 h was necessary, together with repeated adjustment of the pH to 5.5–6 by the addition of 20% NH_4OH solution. The fine-crystalline products that separated out were filtered off, washed with ethanol and dried. The synthesis method used was a version of the method of Melson and Pickering [11]. The products obtained, with colours ranging from light-blue through grey and grey-green to green, are soluble in water, but insoluble in most organic solvents.

Elemental analysis

The coordination compounds were subjected to quantitative analysis: the metal contents were determined by atomic absorption techniques, and the carbon and hydrogen contents by using a combustion method coupled with chromatographic techniques.

Spectral measurements

The UV-VIS reflectance spectra were recorded at room temperature on a Specord M 40 spectrophotometer, in the range 11.000–54.000 cm^{-1}.

The IR spectra of the polynuclear compounds were obtained by applying the KBr pellet technique in the range 400–4.000 cm^{-1}, using a Specord M-80 infrared spectrophotometer.

X-ray powder diffraction

The state of crystallinity of the compounds used and the decomposition products were investigated by means of a Dron 3 X-ray diffractometer, with CoK_α radiation.

Thermal measurements

The thermal decomposition curves were investigated with a Q-1500 D Paulik-Paulik-Erdey derivatograph in a static air atmosphere at heating rates in the range 2.5–5 K min^{-1}, with a sample mass of 50 mg, in ceramic crucibles, with α-Al_2O_3 as reference compound. The values of non-isothermal kinetic parameters were obtained by processing the thermogravimetric data with the program VERSATIL [12], which allows selection of the probable mechanism and evaluation of the corresponding activation parameters.

Magnetic measurements

In order to determine the magnetic susceptibility and the saturation magnetization at room temperature, a Faraday balance was used with $HgCo(SCN)_4$ as calibrant (χ_g=16.44 10^{-6} c.g.s. units).

Results and discussion

Characterization of coordination compounds

The molecular formulae of the polynuclear coordination compounds were demonstrated by means of elemental chemical analysis, together with physicochemical measurements, to be $LnCr(tartrate)_3 \cdot nH_2O$, where *Ln*(III) = La–Er.

The IR spectra confirmed the compositions of the investigated compounds. The IR spectra of all the prepared complexes were very similar (Fig. 1, curve a depicts the IR spectrum of the Er compound). Three absorption regions are of importance:

3500–3100 cm^{-1}. All the compounds exhibit a strong and very wide band (maximum at 3400 cm^{-1}), which may be assigned to the OH stretching vibration of water and the secondary alcohol group.

1600–1300 cm^{-1}. This region is characterized by the presence of the $\nu_{COO^-_{sim}}$ (~1600 cm^{-1}) and $\nu_{COO^-_{sim}}$ (~1380 cm^{-1}) vibration modes characteristic of the coordination of the carboxylic group. The absence of the band at 1700 cm^{-1}, assigned to the carboxylic group in the free acid, suggests the coordination of both COO^- groups to the metal ions.

1200–1000 cm^{-1}. This region is characterized by the vibration frequency of the OH groups. The presence in the spectra of a doublet at 1060 and 1110 cm^{-1} proves that the two C–OH groups are coordinated dissimilarly, as in other analogous compounds [13–15], to two different metal ions (Cr and Ln). This splitting may be attributed to the difference in the vibration energies of the OH groups coordinated to the chelate rings.

Data on the stereochemistry of the metal ions were obtained from the electronic spectra (Fig. 2 and Table 1). The spectra of the Nd(III) and Er(III) compounds were chosen for discussion, as these ions exhibit absorption bands in the visible region. The bands characteristic of the f–f transitions from the fundamental state to an excited one are very sharp and with low intensities, being covered by the large, intense ones characteristic of Cr(III)s. In the electronic spectra, the bands corresponding to Ln(III) are found as shoulders. Recording of the second-

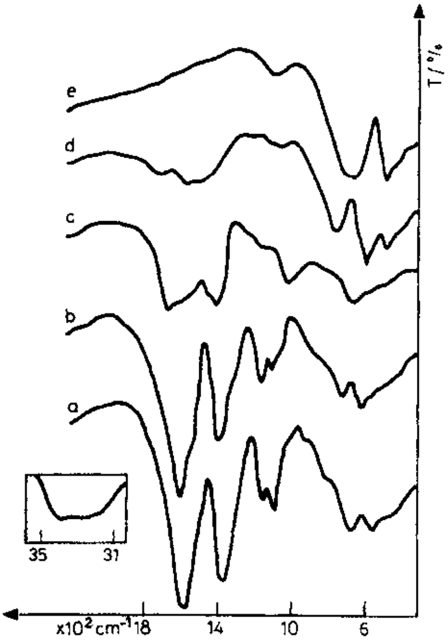

Fig. 1 IR spectra of polynuclear coordination compound ErCr(tartrate)$_3$·10H_2O and its decomposition products. curve a. polynuclear coordination precursor; curve b. dehydrated compound; curve c. oxalate-tartrate intermediate; curve d. intermediate oxocarbonate; curve e. end mixed oxides

order derivatives revealed the bands characteristic of Ln(III)s and Cr(III) in an octahedral configuration.

The values of the magnetic moments of the investigated coordination compounds are given in Table 2. For the Cr–La coordination compound, the value of 3.41 MB is in agreement with the literature data concerning octahedral Cr coordination compounds (μ_{La}+3=0). For the other coordination compounds, the magnetic moments are lower than those obtained by summing the magnetic moments of the paramagnetic metal ions, indicating antiferromagnetic interactions, generally present in such polynuclear coordination compounds.

Thermal decomposition of the polynuclear coordination compounds

In general, all the prepared complexes containing 6–10 water molecules were thermally stable between 22 and 78–88°C. However, the coordination compound containing La displayed stability to only 59°C.

Thermal decomposition data on the coordination compounds [LnCr(tartrate)$_3$]·nH$_2$O, where *Ln*(III) = La, Nd, Eu, Dy and Er, are listed in Table 3.

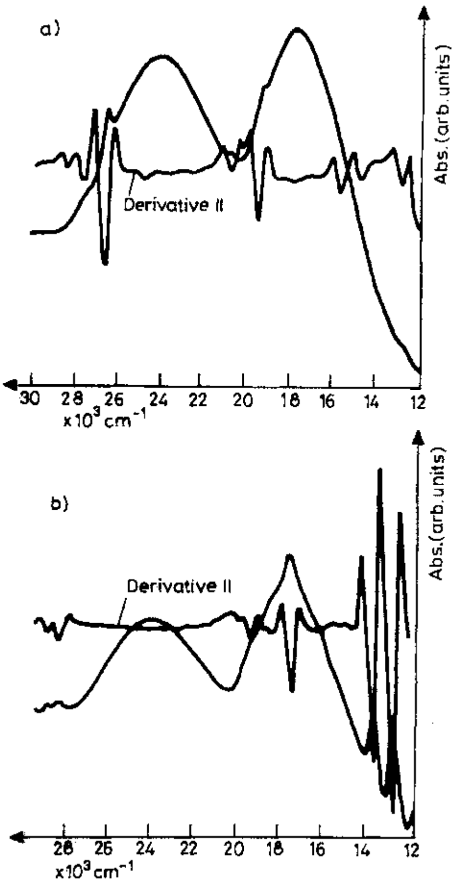

Fig. 2 Electronic spectra of polynuclear coordination compound NdCr(tartrate)$_3$·8H$_2$O (a), ErCr(tartrate)$_3$·10H$_2$O (b)

On the gradual increase of temperature, the coordination compounds lose water in two steps. This multistep dehydration suggests that the water molecules are bonded in various modes. The water lost at lower temperatures is outer sphere water, while that lost at higher temperatures is probably inner sphere water [16]. While the first step is characterized by a temperature at which the reaction rate is maximum and a strong endothermic effect, for the second one a constant rate of mass loss and a weak endothermic effect are typical.

From the TG curves, the activation parameters of dehydration (activation energy E and pre-exponential factor A) were calculated by the Coats-Redfern [17, 18] and Flynn-Wall [19] methods. The results obtained are listed in Table 4. Taking into account the compensated change in the activation parameters, and also

Table 1 Electronic transitions of the metal ions present in the coordination compounds

Coordination compound	Wavenumber/cm^{-1}	Transition
[NdCr(tartrate)$_3$]·8H$_2$O	24 600	
	23 800	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	20 040	$^4I_{9/2} \rightarrow {}^4G_{9/2}$
	19 600	$\rightarrow {}^2G_{9/2}$
	19 080	$\rightarrow {}^4G_{7/2}$
	17 200	$^4A_{2g} \rightarrow {}^4T_{2g}$
	16 800	$^4I_{9/2} \rightarrow {}^4G_{2/2}$
	16 120	$\rightarrow {}^2H_{11/2}$
	13 880	$\rightarrow {}^4F_{9/2}$
	13 440	$^4A_{2g} \rightarrow {}^2T_{2g}, {}^2E_g\}$
	12 960	$^4I_{9/2} \rightarrow {}^4F_{7/2}$
	12 480	$\rightarrow {}^4F_{5/2}$
	12 040	$\rightarrow {}^4F_{3/2}$
[ErCr(tartrate)$_3$]·10H$_2$O	27 400	$^4I_{15/2} \rightarrow {}^2G_{9/2}$
	26 400	$\rightarrow {}^2G_{11/2}$
	24 600	$\rightarrow {}^2H_{9/2}$
	23 600	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	20 840	$^4I_{15/2} \rightarrow {}^4F_{5/2}$
	20 480	$\rightarrow {}^4F_{7/2}$
	19 160	$\rightarrow {}^2H_{11/2}$
	18 280	$\rightarrow {}^4S_{3/2}$
	17 600	$^4A_{2g} \rightarrow {}^4T_{2g}$
	15 280	$^4I_{15/2} \rightarrow {}^4F_{9/2}$
	14 240	$^4A_{2g} \rightarrow {}^2T_{2g}(P), {}^2E_g\}$
	12 440	$^4I_{15/2} \rightarrow {}^4I_{11/2}$

the fact that the reaction orders are practically equal, one can conclude that the decomposition rate is independent of the nature of the rare earth cation.

The initial temperature of the first dehydration step (T_{1i}) and the temperature at which the reaction rate is maximum ($T_{1\,\mathrm{max}}$) change regularly with the atomic number Z.

The third step corresponds to the transformation of tartrate anions to oxalate. For the Eu–Cr and Dy–Cr compounds, the conversion is only partial, leading to LnCr(tartrate)(Ox)$_2$. The third step intermediates are unstable, being converted

Table 2 Magnetic moments of polynuclear coordination precursors and their end-products (thermal treatment: 5 h at 700°C)

Coordination compound	μ/MB	$LnCrO_3$	μ/MB
$[LaCr(tartrate)_3]\cdot 8H_2O$	3.41	$LaCrO_3$	1.98
$[NdCr(tartrate)_3]\cdot 8H_2O$	4.75	$NdCrO_3$	4.10
$[EuCr(tartrate)_3]\cdot 9H_2O$	4.57	$EuCrO_3$	3.99
$[DyCr(tartrate)_3]\cdot 6H_2O$	–	$DyCrO_3$	10.74
$[ErCr(tartrate)_3]\cdot 10H_2O$	10.03	$ErCrO_3$	9.86

into carbonates (Eu–Cr and Dy–Cr coordination compounds) and oxocarbonates (La–Cr, Nd–Cr and Er–Cr coordination compounds). Such oxocarbonate intermediates have already been reported in the decomposition of coordination compounds which contain tartrate as ligand [15, 20–23]. The initial temperature of the third decomposition step (T_{3i}) changes regularly with the atomic number Z, as for the first reaction.

Coordination compound	La–Cr	<	Nd–Cr	<	Eu–Cr	<	Dy–Cr	<	Er–Cr
T_{1i} (°C)	59	<	78	<	81	<	85	<	88
$T_{1\,max}$ (°C)	78	<	81	<	83	<	108	<	130
T_{3i} (°C)	190	<	199	<	200	<	217	<	230

In general, these intermediates undergo further decomposition (2–4 steps) into oxocarbonates with lower contents of carbonate. These intermediates, which remain stable over a relatively extended range of temperature, include:

Table 3 Thermal decomposition data on $[LaCr(tartrate)_3]\cdot nH_2O$

Compound	Stage	$T_{range\,T_i-T_f}$/ °C	T_{max}/ °C	Intermediate	Mass loss/% calcd.	Mass loss/% experim.
$[LaCr(tartrate)_3]\cdot 6H_2O$	I	59–128	78	$LaCr(tartrate)_3\cdot 2H_2O$	13.97	13.82
	II	128–190		$LaCr(tartrate)_3$	4.65	5.01
	III	190–293	263	$LaCrOx_3$	22.51	23.14
	IV	283–322	299	$LaCr(CO_3)_{5/2}O_{1/2}$	13.71	13.33
	V	322–368	335	$LaCr(CO_3)_2O$	2.84	3.01
	VI	368–434		$LaCr(CO_3)_{3/2}O_{3/2}$	2.84	3.14
	VII	434–547	482	$LaCr(CO_3)_{1/2}O_{5/2}$	5.69	5.01
	VIII	740–758	747	$LaCrO_3$	2.84	2.77
				Total loss:	69.05	69.23

Table 3 Continued

Compound	Stage	$T_{\mathrm{range}\,T_i-T_f}$/ °C	T_{max}/ °C	Intermediate	Mass loss/% calcd.	Mass loss/% experim.
[NdCr(tartrate)$_3$]·8H$_2$O	I	78–141	81	NdCr(tartrate)$_3$·2H$_2$O	13.86	13.50
	II	141–199		NdCr(tartrate)$_3$	4.62	4.34
	III	199–295	268	NdCrOx$_3$	22.35	22.07
	IV	295–330	301	NdCO$_3$O$_2$	22.10	22.63
	V	390–545	510	Nd(CO$_3$)$_{1/3}$O$_{8/3}$	3.76	4.00
	VI	688–720	719.5	NdCrO$_3$	1.88	1.74
				Total loss:	68.57	68.37
[EuCr(tartrate)$_3$]·9H$_2$O	I	81–143	83	EuCr(tartrate)$_3$·2H$_2$O	15.67	15.40
	II	143–200		EuCr(tartrate)$_3$	4.47	4.41
	III	200–263		EuCr(tartrate)(Ox)$_2$	14.42	15.00
	IV	263–291	268	EuCr(CO$_3$)$_3$	17.66	18.42
	V	360–440	400	EuCr(CO$_3$)$_2$O	5.47	5.52
	VI	440–508		EuCr(CO$_3$)$_{3/2}$O$_{3/2}$	2.73	2.64
	VII	508–558	544	EuCr(CO$_3$)$_{1/2}$O$_{5/2}$	5.47	5.32
	VIII	726–751	747	EuCrO$_3$	2.73	2.28
				Total loss:	68.62	69.63
[DyCr(tartrate)$_3$]·6H$_2$O	I	85–153	108	DyCr(tartrate)$_3$·1H$_2$O	11.83	12.05
	II	153–217		DyCr(tartrate)$_3$	2.36	2.32
	III	217–300	269	DyCr(tartrate)(Ox)$_2$	15.25	16.02
	IV	300–350	311	DyCr(CO$_3$)$_3$	18.67	18.45
	V	490–605		DyCr(CO$_3$)$_{1/2}$O$_{5/2}$	14.46	13.90
	VI	682–755	739	DyCrO$_3$	2.89	3.02
				Total loss:	65.46	65.76
[ErCr(tartrate)$_3$]·10H$_2$O	I	88–160	130	ErCr(tartrate)$_3$·2H$_2$O	17.19	16.32
	II	160–230		ErCr(tartrate)$_3$	4.29	4.74
	III	230–308	268	ErCrOx$_3$	20.78	19.95
	IV	308–359	318	ErCr(CO$_3$)$_{1/2}$O$_{5/2}$	23.17	23.60
	V	519–577	547	ErCr(CO$_3$)$_{2/6}$O$_{16/6}$	0.87	1.02
	VI	678–730	705	ErCrO$_3$	1.75	1.68
				Total loss:	68.06	67.74

Table 4 Kinetic activation parameters for first reaction step (β=3°C min^{-1})

Compound	Coats-Redfern				Flynn-Wall				Coats-Redfern, modified			
	E/ kJ mol^{-1}	*A*/ s^{-1}	*n**	*r***	*E*/ kJ mol^{-1}	*A*/ s^{-1}	*n*	*r*	*E*/ kJ mol^{-1}	*A*/ s^{-1}	*n*	*r*
[LaCr(tartrate)$_3$]·8H$_2$O	66.3	$1.7\cdot10^{7}$	1.5	–0.994681	60.3	$4.9\cdot10^{7}$	1.5	–0.995535	65.3	$1.2\cdot10^{7}$	1.4	–0.994716
[NdCr(tartrate)$_3$]·8H$_2$O	71.5	$1.1\cdot10^{8}$	1.6	–0.993793	72.8	$1.9\cdot10^{8}$	1.6	–0.994699	73.6	$2.5\cdot10^{8}$	1.6	–0.993603
[EuCr(tartrate)$_3$]·9H$_2$O	76.5	$8.0\cdot10^{8}$	1.6	–0.998159	70.7	$1.2\cdot10^{8}$	1.5	–0.998424	70.4	$8.3\cdot10^{8}$	1.5	–0.998251
[DyCr(tartrate)$_3$]·6H$_2$O	73.5	$5.5\cdot10^{8}$	1.6	–0.998732	74.3	$6.3\cdot10^{8}$	1.6	–0.998955	70.4	$4.8\cdot10^{8}$		–0.998677
[ErCr(tartrate)$_3$]·10H$_2$O	64.2	$7.7\cdot10^{6}$	1.4	–0.998910	66.6	$22.0\cdot10^{6}$	1.4	–0.990952	65.8	$1.4\cdot10^{7}$	1.4	–0.998856

* reaction order

** correlation coefficient of linear regression

$LaCr(CO_3)_{1/2}O_{5/2}$ (547–743°C), $NdCrCO_3O_2$ (330–390°C), $NdCr(CO_3)_{1/3}O_{8/3}$ (545–688°C), $EuCr(CO_3)_3$ (291–360°C), $EuCr(CO_3)_{1/2}O_{5/2}$ (558–716°C), $DyCr(CO_3)_3$ (350–499°C), $DyCr(CO_3)O_{5/2}$ (605–682°C), $ErCr(CO_3)_{1/2}O_{5/2}$ (359–577°C) and $EuCr(CO_3)_{2/6}O_{16/6}$ (577–670°C). The high thermal stability up to 743°C of the intermediate $LaCr(CO_3)_{1/2}O_{5/2}$ is in agreement with the literature data concerning the thermal decomposition of other coordination compounds of La with carboxylic acid ligands [23].

The final stage in the thermal decomposition of the coordination compounds $[LnCr(tartrate)_3]\cdot nH_2O$ is the total transformation of the oxocarbonate intermediates to the corresponding mixed oxides $LnCrO_3$. $NdCrO_3$ is formed at the lowest temperature. The final temperatures of decomposition of the polynuclear coordination compounds (T_f), which correspond to the synthesis of mixed chromites, do not vary gradually with the atomic number Z, but increase in the following sequence:

Mixed oxide	$NdCrO_3$	<	$ErCrO_3$	<	$EuCrO_3$	<	$DyCrO_3$	<	$LaCrO_3$
T_f(°C)	720	<	723	<	751	<	755	<	758

Besides the stoichiometric calculations based on the thermoanalytical curves, the above decomposition mechanism was confirmed by IR spectral investigations, which allow a qualitative identification of the intermediates. The disappearance with increasing temperature of the bands assigned to ν_{C-OH} (1120 and 1050 cm^{-1}) and ν_{C-H} (900 cm^{-1}), characteristic of the presence of tartrate ligands, and the conservation up to ~300°C of the bands specific for the carboxylate anion, indicate the formation of oxalate. The appearance at higher temperatures of the absorption bands assigned to CO_3^{-2} vibrations [24] (1430–1410 cm^{-1} and 825–600 cm^{-1}) prove the above-mentioned reaction stoichiometry. The changes occurring in the IR spectra during the progressive heating of the polynuclear coordination compound $[ErCr(tartrate)_3]\cdot 10H_2O$ are shown in Fig. 1 (curves b–e).

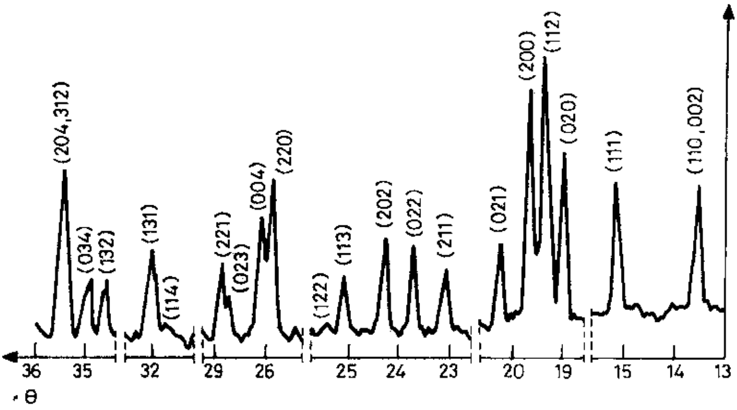

Fig. 3 X-Ray diffractogram of $EuCrO_3$ (thermal treatment: 5 h at 700°C)

Characterization of the end-products of thermal decomposition

The end-products of the thermal decompositions of the investigated coordination compounds corresponded to the molecular formula $LnCrO_3$, specific for orthochromites. Thermal treatment for 5 h at 700°C led to well-crystallized mixed oxides (Fig. 3), as confirmed by X-ray diffraction analysis.

The IR spectra display the vibrations specific for ν_{Cr-O} (at ~600 cm^{-1}), slightly shifted relative to those obtained for Cr_2O_3(~640 cm^{-1}) [25], due to the decrease in the covalent character of the Cr–O bond in orthochromites.

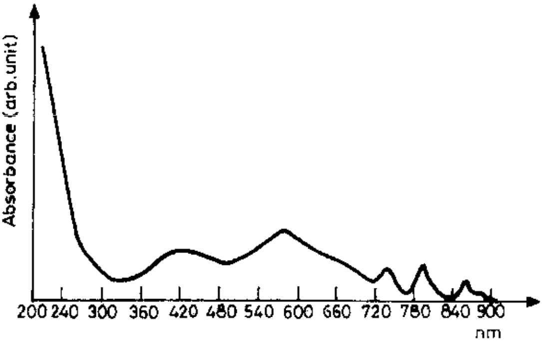

Fig. 4 Electronic spectrum of $EuCrO_3$

The electronic spectra (Fig. 4) demonstrate the bands characteristic of Ln(III) ions, and also the bands specific for Cr(III) in an O_h configuration:

$$\begin{array}{lcll}
{}^4A_{2g} & \rightarrow & {}^4T_{1g}\,(F) & (420\ \text{nm}) \\
{}^4A_{2g} & \rightarrow & {}^4T_{2g} & (580\ \text{nm}) \\
{}^4A_{2g} & \rightarrow & \begin{array}{l}{}^4T_{2g}\\ {}^4A_{2g}\end{array} & \Big\}(734\ \text{nm})
\end{array}$$

The orthochromites are paramagnetic compounds. The magnetic moments of the final products are given in Table 2 and Fig. 2.

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