TABLE III

REDOX REACTIONS AND EQUILIBRIA FOR S_8 IN DMSO AT A GOLD ELECTRODE

	E_p *vs.* sce, V	
	Cathodic	Anodic
$S_8 + e^- \rightarrow S_8^-$	-0.62	
$2S_8^- \rightleftarrows (S_8)_2^{2-}$, $K_f = 5 \times 10^3$ M^{-1}		
$(S_8)_2^{2-} \rightarrow 2S_8 + 2e^-$		-0.23
$S_8^- + e^- \rightleftarrows S_8^{2-}$	-1.29	-1.15
$S_8^{2-} \rightarrow mS_n^{2-/m}$		

measurable effect. Therefore, the molar absorbtivities of the monomer can be evaluated: $a_{\text{monomer}}(618\ \text{m}\mu) = 2.58 \times 10^3\ M^{-1}\ \text{cm}^{-1}$; $a_{\text{monomer}}(490\ \text{m}\mu) = 0.52 \times 10^3\ M^{-1}\ \text{cm}^{-1}$. These molar absorbtivities have been used to determine the dissociation constant and the molar absorptivities for the dimer. The spectra of 12 solutions with total concentrations of "S_8^-" varying from 0.0852 to 4.26 mM have been used to obtain the best fit for the constants. The resulting values are $K = (2 \pm 1) \times 10^{-4}\ M$, $a_{\text{dimor}}(490\ \text{m}\mu) = 5.32 \times 10^3\ M^{-1}\ \text{cm}^{-1}$, $a_{\text{dimer}}(618\ \text{m}\mu) = 2.12 \times 10^3\ M^{-1}\ \text{cm}^{-1}$. The existence of one isosbestic point in Figure 4 indicates that only two species are responsible for the absorbance in this portion of the spectrum.

Summary and Conclusions

The oxidation–reduction reactions of S_8 and its reduction products, as well as their equilibria, are summarized in Table III. These proposals are consistent with the electrochemical and spectroscopic data.

Although the S_8^- and $(S_8)_2^{2-}$ species have not been isolated, the simplicity of the electrochemistry implies that the monomer exists as an eight-membered ring. Recent studies of the anion of heptasulfurimide are pertinent and indicate possibilities for further work in this area.[10] The anion of heptasulfurimide, which is isoelectronic with S_8, has been shown to exist as an eight-membered ring. Preliminary cyclic voltammetric studies of the anion of heptasulfurimide have shown that its electrochemical reduction in DMSO is almost identical with that of S_8. The presence of nitrogen, with its large magnetic moment in the eight-membered ring, should facilitate the structure determination *via* magnetic resonance techniques.

Additional studies are in progress to determine the chemical reactivity of the "S_8^-" species with a variety of inorganic and organic reagents. Preliminary results indicate that there is a significant interaction between transition metal ions and "S_8^-."

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[10] B. A. Olsen and F. P. Olsen, *Inorg. Chem.*, **8**, 1736 (1969), and references therein.

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A Study of the Thermal Decomposition of Europium(III) Oxalate Using the Mössbauer Effect

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The thermal decomposition of $Eu_2(C_2O_4)_3 \cdot 10H_2O$ was investigated using conventional thermal analytical techniques and also optical and Mössbauer spectrographic methods. Contrary to previous investigations, the intermediate in the decomposition of europium(III) oxalate, which has a 1:1:3 composition europium–carbon–oxygen (*i.e.*, Eu–C–3O), is not europium(II) carbonate but is most probably a carbonylcarbonate of trivalent europium, $Eu_2O_2OCOCO_2$. The final intermediate in the decomposition is EuO_2CO_3.

Introduction

Although the thermal decomposition of rare earth oxalates has been extensively studied, there is substantial disagreement among investigators regarding the complex nature of these decompositions. Perhaps of greatest interest are those in which the rare earth ion is known to have a variable valence. Since changes in oxidation state of the metal ion have frequently been observed during the thermal decomposition of transition metal oxalates, it is of interest to investigate such possibilities in the decomposition of rare earth oxalates. Europium(III) is the rare earth ion most readily reduced and Glasner, *et al.*,[1] have suggested that divalent europium is formed as an intermediate in the thermal decomposition of europium(III) oxalate. However, thermodynamic considerations similar to those of Dollimore, *et al.*,[2] indicate that divalent europium should not form.

The unequivocal determination of the formation of europium(II) in such a complicated decomposition from thermal analysis data alone is difficult. Fortunately,

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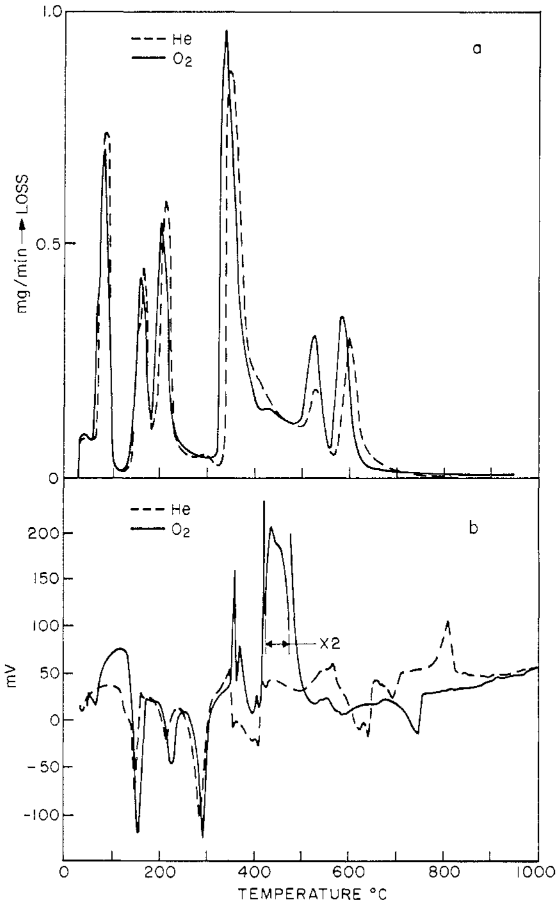

Figure 1.—Thermal analysis curves for $Eu_2(C_2O_4)_3 \cdot 10H_2O$. (a) Differential thermogravimetric analysis: O_2, —; He, - - -. (b) Differential thermal analysis: O_2, —; He, - - -.

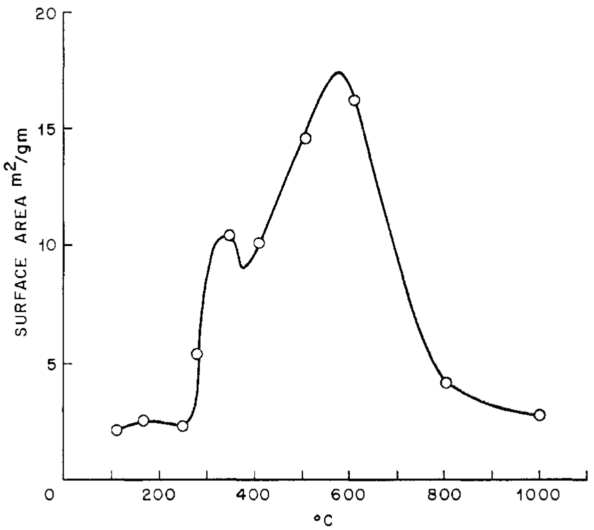

Figure 2.—Surface area of $Eu_2(C_2O_4)_3 \cdot 10H_2O$ calcined in air.

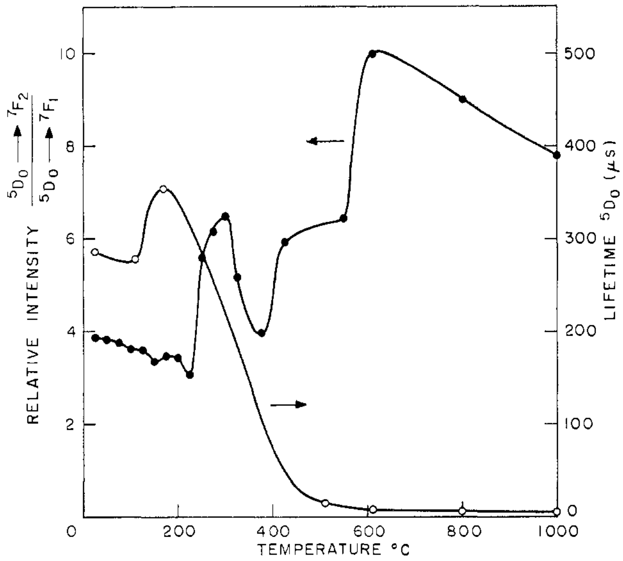

Figure 3.—Emission properties of $Eu_2(C_2O_4)_3 \cdot 10H_2O$ as a function of temperature: left ordinate, relative intensity ratio of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$; right ordinate, lifetime of the $^5D_0$ state.

europium is amenable to Mössbauer spectroscopy which can be used to establish the oxidation state at various stages during the decomposition. This technique has previously been successfully applied, in combination with conventional thermal analysis, to an investigation of changes in the valence of iron during the thermal decomposition of some iron oxalate compounds.[3,4]

Similarly the emission and absorption or reflection spectra of the europium ion can be used to distinguish the oxidation state. In addition, certain inferences regarding the symmetry and bonding of europium(III) ions can be made particularly from the emission spectrum.[5,6] Infrared absorption spectra may also help to define the carbon–oxygen bonding at stages in the decomposition but are less useful in directly determining the oxidation state of the europium ions.

Experimental Procedure and Results

Europium(III) oxalate decahydrate was prepared by homogeneous precipitation from europium(III) chloride solution using ethyl oxalate. The material was air dried.

The thermogravimetric (tga) experiments were performed with a Cahn RG balance modified so as to provide for up to ten automatic range changes. This was accomplished by using recorder limit switches and a stepping motor which provided the automatic steps. The circuit allowed for the substitution of one to nine precision 100-ohm resistors in place of the 1-kilohm helipot which is normally part of the Cahn balance circuit. The results were displayed on a two-pen recorder along with the thermocouple output. Tga runs were made in flowing O_2 and He and under vacuum, at heating rates of 100°/hr. Samples were approximately 100 mg in size and were arranged in a thin unpacked layer on the platinum sample dish. A Fisher differential thermalyzer was used in conjunction with a Leeds and Northrup amplifier and X-Y recorder to obtain the differential thermal analysis (dta) curves. Dta experiments were performed in flowing O_2 and He at 10°/min.

The results of the tga and dta analysis are shown in Figure 1 for the runs in O_2 and He and summarized in Table I. The derivatives of the tga traces (dtga) are presented for ease in determining the steps in the decomposition. The curves are determined by taking the change in weight for 5-min intervals and plotting this against the average temperature during that interval. A computerized technique has been developed since these experiments.[7]

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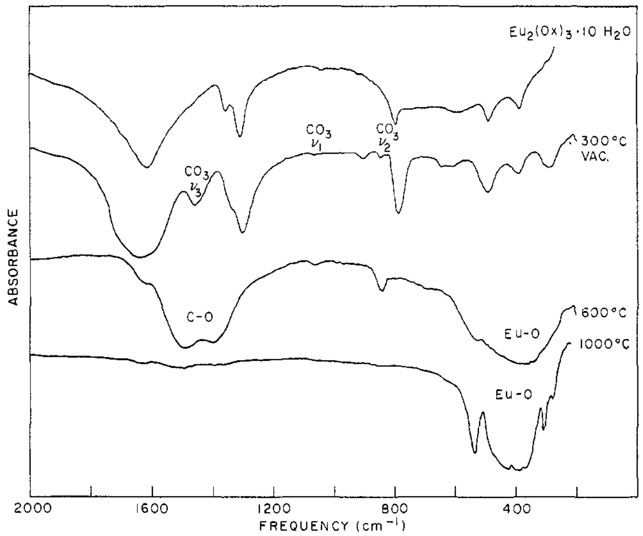

Figure 4.—Infrared spectra of $Eu_2(C_2O_4)_3 \cdot 10H_2O$ calcined at various temperatures under vacuum.

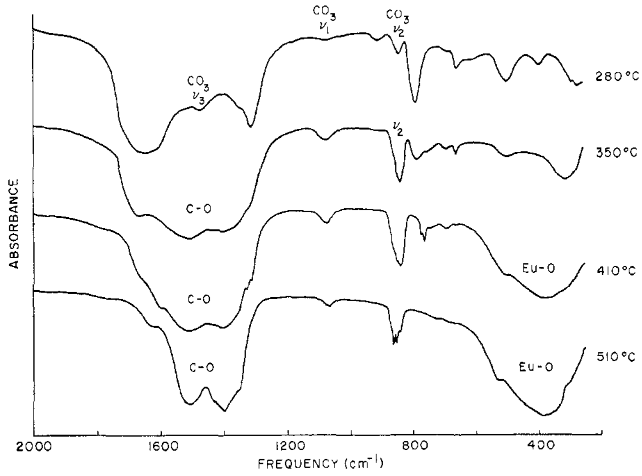

Figure 5.—Infrared spectra of $Eu_2(C_2O_4)_3 \cdot 10H_2O$ calcined at various temperatures under vacuum.

Five-gram samples of $Eu_2(C_2O_4)_3 \cdot 10H_2O$ were calcined in air at temperatures from 100 to 1000° for 30 min and cooled rapidly to room temperature. These samples were then submitted to X-ray diffraction, BET surface analysis, and emission and Mössbauer spectroscopy. The surface area measurements are presented in Figure 2.

A Cary Model 14 recording spectrophotometer was modified[5] for the fluorescence measurements. Spectra taken above room temperature were obtained using a vacuum furnace constructed to conform to the outside shell of an Air Products Cryotip dewar. The rubber O-ring seals were water cooled. Suprasil quartz windows were used. A 600-W cartridge heater was controlled by a Leeds and Northrup controller using a chromel–alumel thermocouple. The vacuum measured at the Veeco VS-9 pumping station under continuous pumping was approximately 5×10^{-6} Torr. This suggests that there was some air leakage but the vacuum was more than adequate for thermal insulation. The change in the ratio of the $^5D_0$–$^7F_2$ to $^5D_0$–$^7F_1$ fluorescence is plotted in Figure 3. The points below 375° were obtained at the indicated temperature while those at 375° and above were room-temperature measurements of the calcined samples. The fluorescent lifetime of the $^5D_0$ state was measured[8] for the calcined samples and the results are also shown in Figure 3. No emission for divalent europium was ever observed during the decomposition of europium(III) oxalate.

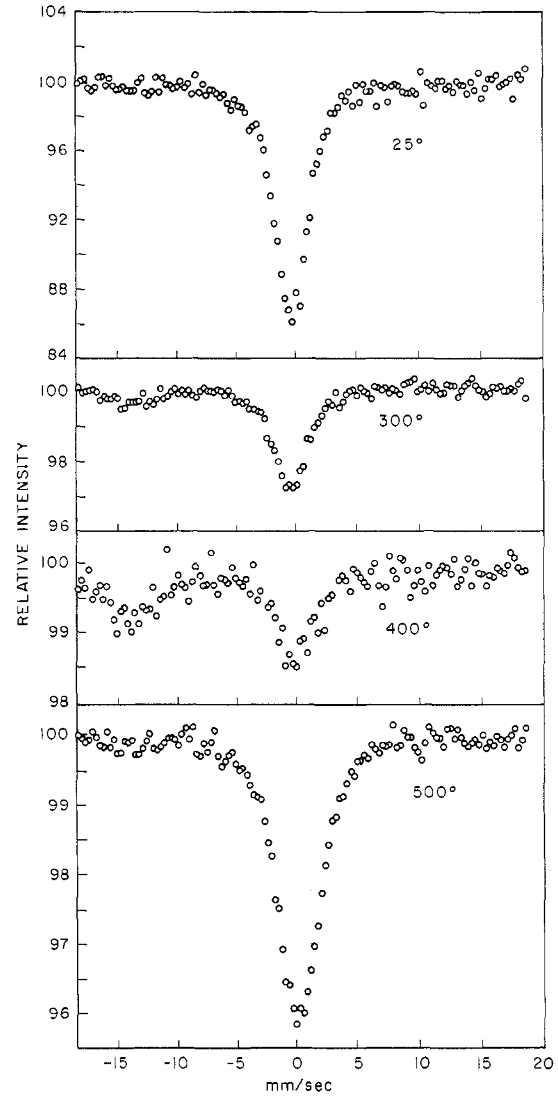

Figure 6.—Mössbauer spectra of $Eu_2(C_2O_4)_3 \cdot 10H_2O$.

Infrared absorption spectra were recorded on a Model 421 Perkin-Elmer spectrophotometer. Samples were run from 2000 to 250 cm^{-1} using the KBr-disk technique with a KBr window in the reference beam. The instrument was continuously purged with dry nitrogen to eliminate atmospheric water and carbon dioxide spectra. Figures 4 and 5 present the results of 2-g samples of $Eu_2(C_2O_4)_3 \cdot 10H_2O$ which had been heated for 0.5 hr under vacuum (10^{-5} Torr) at the temperature indicated. These calcining conditions more closely simulate subsequent Mössbauer measurements and should more readily yield a divalent intermediate than the previously described calcination in air.

A constant-acceleration Mössbauer apparatus similar to that described by Wertheim[9] was employed and the source was Sm_2O_3 containing ^{151}Sm. Calibration was based on the ground-state splitting of ^{57}Fe and a value of 3.92 mm/sec was used from nmr measurements.[10,11] Spectra of the samples which had been calcined in air were measured at room temperature. These did not show any evidence of divalent europium. The vacuum furnace described previously was used to obtain the Mössbauer spectra at elevated temperatures. The quartz windows were replaced with 3-mil Mylar and an aluminum foil radiation shield, and sample containers were employed. Europium(III) oxalate decahydrate was studied from room temperature to 600°. Figure 6 shows selected spectra.

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TABLE I
SUMMARY OF WEIGHT LOSS DATA FOR $Eu_2(C_2O_4)_3 \cdot 10H_2O$

			O_2		He		Vacuum (2×10^{-3} Torr)	
Product	Loss	Theoret %	Temp, °C	%	Temp, °C	%	Temp, °C	%
$Eu_2(C_2O_4)_3 \cdot 6H_2O$	$4H_2O$	9.6	30–110	9.9	30–110	10.0	25	10.3
$Eu_2(C_2O_4)_3 \cdot 4H_2O$	$2H_2O$	14.4	115–180	15.5	120–175	14.4	...	...
$Eu_2(C_2O_4)_3$	$4H_2O$	24.1	180–310	24.1	180–310	24.1	25–305	24.1
Eu–C–3O	$2CO_2$, 2CO	43.3	310–490	43.4	310–490	44.1	305–460	45.1
$Eu_2O_2CO_3$	CO	47.1	490–560	47.7	490–565	47.8	460–560	49.8
Eu_2O_3	CO_2	53.0	560–925	52.8	565–800	53.0	560–1012	53.0

Discussion

The proposed scheme of decomposition is inferred by the losses indicated in Table I. The dehydration of the decahydrate proceeds in steps of 4–2–4 as inferred from the three endothermic peaks in the dta traces and the three weight loss peaks in the dtga curves in Figure 1. The weight losses agree well with the theoretical values as shown in Table I.

The next step in the decomposition is the critical one as it involves the formation of europium(II) carbonate according to Glasner, *et al.*[1] Certainly this is a logical choice based upon the weight loss data presented in Table I. It is not substantiated, however, by the results of the emission spectra and X-ray diffraction patterns of the calcined samples and is completely contradictory to the Mössbauer spectra of these same samples. Although there are uncertainties involved in the comparison of static and dynamic measurements, the agreement is sufficiently good in the other aspects of the decomposition and consequently it is felt that they are also significant regarding the absence of europium(II) carbonate. There is continuous fluorescence associated with trivalent europium as indicated in Figure 3 and there is no fluorescence observed for divalent europium.[6] The X-ray diffraction patterns of samples calcined at 410 and 510° are admittedly broad and diffuse but nevertheless do not show any of the prominent lines of europium(II) carbonate[12] or of a sample of europium(II) carbonate which has been heated to 450°. The patterns for samples calcined at 700° and above reveal only lines expected for europium(III) oxide.

The Mössbauer spectra of the samples which were calcined in air also do not show evidence of divalent europium. The minimum in the dtga curves which corresponds to the formation of the species in question (Eu–C–3O) is as prominent in oxygen as under vacuum or helium. It is concluded, therefore, that the same entity exists regardless of atmosphere and that the intermediate formed at this stage during the normal decomposition is not europium(II) carbonate.

On the other hand, it is certainly possible to conduct the decomposition in an atmosphere which is sufficiently reducing to form some divalent europium. This is evident from Figure 6 which shows the formation of considerable divalent europium as indicated by the absorption at −14 mm/sec. This divalent europium is presumed to result from the reduction of the sample under vacuum at elevated temperatures in the presence of reactive carbon formed by the disproportionation of carbon monoxide. The subsequent reoxidation is explained in terms of the eventual exhaustion of carbon and europium(II) by the small amount of air leakage during the time (~24 hr) necessary to come to temperature equilibrium and obtain favorable counting statistics. The vacuum present in the Mössbauer dewar is substantially better than that present during the vacuum tga as given elsewhere. It is maintained that divalent europium formed in this or a related manner is not an intermediate in the actual decomposition of europium(III) oxalate in the same fashion that iron(II) or nickel metal are in the decomposition of iron(III) and nickel(II) oxalates.

Effluent gas analysis should help to determine the nature of this intermediate. However, the relative amounts of carbon monoxide and dioxide evolved are not subject to quantitative interpretation due to the unknown extent of disproportionation of carbon monoxide at these temperatures.

The reaction has unfavorable kinetics as evidenced by the room-temperature stability of carbon monoxide; however, it is reasonable to assume that the decomposition products will have a catalytic effect.[13] In fact the reaction has been demonstrated to occur extensively during the decomposition of a variety of oxalates.[1,3,14]

A possible intermediate species which has the proper stoichiometry and trivalent europium is the dioxyoxalate $Eu_2O_2C_2O_4$. Since planar and nonplanar oxalate ions have been shown to have different decomposition rates,[15] this appears to be a reasonable choice. The infrared spectra in Figure 4, however, indicate the demise of the oxalate bands around 790, 1315, and 1650 cm^{-1} and the appearance of the carbonate bands around 840, 1080, and 1480 cm^{-1} in the temperature interval between 300 and 600°. Figure 5 explores this region in greater detail and it is obvious that the species under consideration has oxide and carbonate absorption bands and not those of the oxalate ion.

In their study of the kinetics of oxalate ion pyrolysis, Hartman and Hisatsune[16] have proposed that the decomposition occurs *via* a carbon dioxide anion free radical. They further speculated that a possible transition complex is a carbonylcarbonate ion $OCOCO_2^{2-}$. The intermediate compound $Eu_2O_2OCOCO_2$ has the proper stoichiometry and valence of europium and would be expected to exhibit the infrared absorption

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(16) K. O. Hartman and I. C. Hisatsune, *ibid.*, **71**, 392 (1967).

peaks corresponding to the carbonate ion. On the basis of the available evidence this is the proposed intermediate at about 500° in the thermal decomposition of europium(III) oxalate.

The transient complex then loses carbon monoxide to form the dioxycarbonate compound $Eu_2O_2CO_3$. This is in agreement with Glasner, *et al.*,[1] and dioxycarbonate has been observed in the decomposition of many of the rare earth oxalates,[17,18] carbonates,[19] and acetates.[20]

The final step in the decomposition is the slow evolution of carbon dioxide to form europium(III) oxide.

The dependence of surface area upon calcining temperature, shown in Figure 2, is completely consistent with this proposed scheme of decomposition. The initial peak in surface area around 300° is the result of the final stage of dehydration and there is a slight decrease in surface area after this due to some healing over of the cracks and channels produced in the aggregates by the evolution of water. The major decomposition leads to a large broad peak in surface area around 500° as a result of the major disruption of the crystallites by the evolution of gas and conversion to the oxide. The resulting aggregates of finely divided oxide tend to sinter rapidly and grow, leading to a steep decrease in surface area beyond 600°. This behavior is very similar to that observed by Subbarao, *et al.*, for cerium(III)[21] and neodymium oxalates.[22]

The emission spectra summarized in Figure 3 also reflect the course of the decomposition. Both the lifetime and the intensity of the $^5D_0 \rightarrow {}^7F_1$ fluorescence are dependent upon the opportunity for nonradiative decay of the excited $^5D_0$ state. The intensity of the $^5D_0 \rightarrow {}^7F_2$ emission, however, is also very dependent upon the symmetry in the environment of the europium ion. This has been adequately demonstrated for solutions,[5,23] glasses,[6] and solids.[24] Therefore, the ratio of intensities for the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition would reflect the symmetry and order in the material, and consequently it should peak at highly disordered and disrupted portions during the decomposition. The similarity between the ratio as plotted in Figure 3 and the surface area curve in Figure 2 is obvious and reasonable. The lifetime of the $^5D_0$ shows a continuous decrease to the value characteristic of europium(III) oxide. This may be a simple result of decrease in Eu–Eu distances in the structure leading to increased self-quenching.

Conclusions

The dehydration of $Eu_2(C_2O_4)_3 \cdot 10H_2O$ proceeds in steps of 4–2–4 molecules of water. The decomposition of the anhydrous material proceeds *via* an intermediate having the composition Eu–C–3O, but it is not europium(II) carbonate. It is proposed that it is a carbonylcarbonate $Eu_2O_2OCOCO_2$. This intermediate loses carbon monoxide and forms the dioxycarbonate $Eu_2O_2CO_3$ which finally forms europium(III) oxide with the evolution of carbon dioxide. The surface area and fluorescence spectra show two areas of disordered structure which correspond to the final dehydration step and the combined oxalate and carbonate decomposition.

Mössbauer spectra are useful to establish unequivocally the oxidation state throughout the decomposition and the observed spectra are consistent with the proposed schemes of decomposition.

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