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Synthesis, Structure, and Catalytic Properties of Rare-Earth Ternary Sulfates

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Three rare-earth ternary sulfates $NaM(SO_4)_2 \cdot H_2O$ (M = La, Nd, and Gd) have been hydrothermally synthesized, and the crystal structures of the three compounds have been solved by single-crystal X-ray diffraction. The lanthanum and neodymium sulfates show the space group $P3_121$ while the gadolinium compound presents the enantiomer $P3_221$. The three lanthanum, neodymium, and gadolinium sulfates have been tested as heterogeneous redox catalysts in the selective oxidation of sulfides, showing good activities and selectivities. They can be reused without loss of yield or selectivity.

1. Introduction

As a part of our systematic search for novel inorganic catalysts and following our work on rare-earth sulfates[1] and sulfonates,[2] we are now focusing our research on the catalytic properties of hydrated rare-earth ternary sulfates $NaM(SO_4)_2 \cdot H_2O$. There are many known ternary rare-earth sulfate hydrates with alkaline metal or NH_4^+ ions as the third component.[3] Among them, the compounds with general formula $AM(SO_4)_2 \cdot nH_2O$ are the best studied: with the beginning of the 1970s, the crystal structures of many of these compounds were determined, and today, more than 30 structures are known.[4−25] The crystal structures of the monohydrated sodium compounds have only been determined for M = La[4] and Ce,[5,7] but powder diffraction results showed the fact that the respective sulfates with the smaller M^{3+} ions down to Er were isostructural.[26] The $NaM(SO_4)_2 \cdot H_2O$ sulfates have been described with the enantiomorphic space group $P3_121$ and additionally, for $NaCe(SO_4)_2 \cdot H_2O$, the second enantiomorph with the space group $P3_221$ has been reported.[7] The thermal behavior of the $NaM(SO_4)_2 \cdot H_2O$ compounds with M = La, Ce, Nd, and Sm has been studied in great detail in order to determine the decomposition kinetics.[27] However, the catalytic properties of the sulfates have been scarcely investigated.[1] Our interest in these materials lies in the study of the relation between their structure and their potential application as redox catalysts in the oxidation of sulfides to produce sulfoxides. Sulfoxides are important intermediates of many natural products.[28] Their synthesis has been achieved by means of a wide range of oxidizing systems, starting from the corresponding sulfides, with aqueous hydrogen peroxide. H_2O_2 is a particularly attractive oxidant since it is cheap, environmentally friendly, and easy to handle and produces only water as a byproduct, which reduces purification requirements. The catalysts, often used to enhance the efficiency of the oxidation, are mostly metal salts (chlorides, oxides, peroxides, acetates, and acetyl acetonates of Ti, V, Mo, W, Re, and Mn). They play a very important role as catalytic activators of hydrogen peroxide:

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10.1021/cm049451z CCC: $30.25

Table 1. Crystal Data and Structure Refinement for 1, 2, and 3

	1	2	3
formula	$NaLa(SO_4)_2 \cdot H_2O$	$NaNd(SO_4)_2 \cdot H_2O$	$NaGd(SO_4)_2 \cdot H_2O$
CSD deposition number	414450	414449	414448
temperature (K)	296	296	296
molar weight (g/mol)	372.04	377.37	390.38
crystal system	trigonal	trigonal	trigonal
space group	$P3_121$	$P3_121$	$P3_221$
$a = b$ (Å)	7.0538(5)	6.968(2)	6.8816(6)
c (Å)	12.963(1)	12.856(6)	12.770(2)
cell volume (Å^3)	558.55(8)	540.6(4)	523.7(1)
Z	3	3	3
calc. density (g/cm^3)	3.318	3.478	3.713
μ (mm^{-1})	6.377	7.866	10.181
dimensions (mm)	0.50 × 0.20 × 0.10	0.02 × 0.02 × 0.02	0.25 × 0.25 × 0.02
radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
diffractometer	Bruker-SMART-CCD	Bruker-SMART-CCD	Bruker-SMART-CCD
limiting indices	(−7, −9, −17) to (9, 7, 18)	(−7, −9, −17) to (9, 5, 18)	(−9, −9, −18) to (9, 9, 14)
θ range for data collected	4.59−31.13	3.73−31.01	3.77−31.17
reflections collected	4245	4056	3759
independent reflections	1136	1099	1068
$R[I > 2\sigma(I)]$	0.0362	0.0313	0.0519
$wR(F^2)$	0.0694	0.0542	0.0868
absorption correction	sadabs	sadabs	sadabs
flack parameter	0.01(4)	0.02(3)	−0.04(5)

the resulting metal-peroxo derivatives are such powerful catalysts that usually give rise to over-oxidized byproducts. Lanthanides have scarcely been explored in the oxidation of thioethers, yet these elements are receiving increasing attention in the literature.[29]

In this work, we report the synthesis, crystal structures, and catalytic activity on sulfide oxidation of three sulfates $NaM(SO)_4 \cdot H_2O$ with M = La, Nd, and Gd.

2. Experimental Section

Synthesis. Although most sulfates have been obtained in solution or in the solid state (through decomposition or sintering) and in melts,[30] hydrothermal conditions have provided good yields, short reaction times, and high purity in the synthesis of the compounds $NaLa(SO)_4 \cdot H_2O$, $NaNd(SO_4)_2 \cdot H_2O$, and $NaGd(SO_4)_2 \cdot H_2O$ (hereafter named **1**, **2**, and **3**, respectively). In particular, **1** and **2** had been previously prepared by dissolving the corresponding rare-earth oxide in 1 M H_2SO_4, adding distilled water to obtain a 0.05 M solution, mixing with a 5-fold excess of Na_2SO_4, and leaving for several days until they crystallized.[27b] Another synthetic method found in the literature for $NaLa(SO)_4 \cdot H_2O$ involved a 3-week gel-diffusion growth[4] since direct mixing of aqueous solutions of lanthanum and sodium sulfates produced crystals too small for single-crystal X-ray diffraction. In our case, the sulfates were obtained under hydrothermal conditions by the reaction of M^{3+} ions with 1,5-benzenedisulfonic acid disodium salt in a 2:3 ratio, in a short reaction time (24 h), as crystalline single phases suitable for single-crystal X-ray diffraction. The reaction conditions cause the benzenedisulfonic acid to undergo hydrolysis and release the SO_4 groups, giving rise to $NaM(SO)_4 \cdot H_2O$ sulfates. All reagents were commercially available and used as received. In every case, 1 mmol of $M(NO_3)_3 \cdot 6H_2O$ (M = La, Nd, Gd) and 1.5 mmol of benzenedisulfonic acid disodium salt were mixed in 5 mL of distilled water. After the pH value was adjusted to 7−8 by addition of triethylamine, the reaction mixture was stirred to homogeneity in a 25 mL PTFE bottle and sealed in a stainless steel autoclave (PARR, USA). The reaction was carried out at 180 °C for 24 h under autogenous pressure and cooled afterward. The solids were filtered off, washed thoroughly with distilled water, ethanol, and acetone, and finally dried at room temperature. The resulting products were obtained in every case as single phases of colorless (compounds **1** and **3**) or mauve (compound **2**) transparent prismatic crystals.

Structure Determination. Single Crystal X-ray Diffraction. A summary of the conditions for data collection is given in Table 1. Transparent prismatic crystals of **1**, **2**, and **3** were mounted on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 20 mA. Data were collected over a hemisphere of reciprocal space by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 20 s covered 0.3° in ω. The crystal-to-detector distance was 5.09 cm. Coverage of the unique set was over 99% complete to at least 23° in θ. Unit cell dimensions were determined by a least-squares fit of 60 reflections with $I > 20\sigma(I)$. The first 100 frames of data were recollected at the end of the data collection to monitor crystal decay. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for S, Gd, La, and Nd were taken from the *International Tables for Crystallography*.[31] The structures were solved by Patterson methods and refined in the $P3_121$ (compounds **1** and **2**) and $P3_221$ (compound **3**) groups. In the three sulfates, the hydrogen atom from the water molecule was located in a difference Fourier synthesis and included in the refinement. All calculations were performed using SMART software for data collection, SAINT[32] for data reduction, SHELXTL™ [33] to resolve and refine the structure and to prepare material for publication, and ATOMS[34] for molecular graphics.

X-ray Powder Diffraction. The X-ray powder diffraction patterns were taken at room temperature using a Siemens D-500 diffractometer in the step scan mode, Cu Kα ($\lambda = 1.540598$ Å) radiation, at a step value of 0.02°, measuring for 0.2 s at each step.

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $NaLa(SO_4)_2 \cdot H_2O$ (Regular Characters), $NaNd(SO_4)_2 \cdot H_2O$ (Bold), and $NaGd(SO_4)_2 \cdot H_2O$ (Italic)

	x	*y*	*z*	*U*(eq)[a]
M (1)	0.56735(8)	0.56735(8)	0	105(1)
	0.5646(1)	**0.5646(1)**	**0**	**79(1)**
	0.56586(7)	*0.56586(7)*	*0*	*98(2)*
S (1)	0.5600(3)	0.5474(3)	0.75332(9)	119(3)
	0.5585(2)	**0.5458(2)**	**0.75580(1)**	**89(2)**
	0.5454(4)	*0.5579(5)*	*−0.2422(2)*	*109(4)*
O (1)	0.4956(9)	0.3630(9)	0.8257(3)	210(12)
	0.4922(7)	**0.3592(7)**	**0.8280(2)**	**142(9)**
	0.486(1)	*0.352(1)*	*0.1688(5)*	*180(20)*
O (2)	0.6109(7)	0.7406(7)	0.8184(3)	180(11)
	0.6120(6)	**0.7397(6)**	**0.8222(3)**	**168(9)**
	0.741(1)	*0.612(1)*	*−0.1748(5)*	*167(18)*
O (3)	0.4090(8)	0.1637(8)	0.0262(4)	206(12)
	0.4111(6)	**0.1660(6)**	**0.0284(3)**	**145(9)**
	0.170(1)	*0.413(1)*	*0.0298(6)*	*152(18)*
O (4)	0.4975(9)	0.8821(9)	0.0137(3)	195(12)
	0.4954(7)	**0.8772(8)**	**0.0156(3)**	**146(10)**
	0.872(1)	*0.496(1)*	*0.0169(5)*	*133(19)*
O (5)	0.930(1)	0.930(1)	0	580(40)
	0.923(1)	**0.923(1)**	**0**	**490(30)**
	0.922(2)	*0.922(1)*	*0*	*470(60)*
Na (1)	0	0.4700(6)	0.1667	228(8)
	0	**0.4694(6)**	**0.1667**	**203(7)**
	0.4688(9)	*0*	*0.1667*	*165(12)*

[a] *U*(eq) is defined as one-third of the trace of the orthogonal $\mathbf{U}_{ij}$ tensor.

Powder diffraction results were used to check the purity of the microcrystalline powder by comparison of the experimental measures with the simulated X-ray powder patterns obtained from the single-crystal X-ray diffraction data.

Catalytic Reactions. Sulfide oxidation reactions were carried out in a 25 mL flask equipped with a magnetic stirrer. In a typical experiment, a suspension of the catalyst (0.015 mmol) in acetonitrile (5 mL) was stirred with a solution of the corresponding thioether (methylphenylsulfide or (2-ethylbutyl)phenylsulfide, 0.3 mmol). The oxidant, H_2O_2 (30%, 1.5 or 1.0 mmol), was added dropwise while the overall suspension was heated at 40 °C. Samples were taken every hour and analyzed after filtration. Chemical yields of sulfoxides and sulfones were measured by gas chromatography (GC) with a chiral glass capillary column of 15/85 mixture of methylsilicone (OV-1701) and methylsilicone-heptakis-[2,3-dipentyl-6-(*tert*-butyldimethylsilyl)]-β-cyclodextrin as stationary phase.[35] GC was performed in a Hewlett-Packard 5890 II chromatograph equipped with a flame ionization detector in a cross-linked methylsilicone column.

3. Results and Discussion

Crystal Structure. A summary of the fundamental crystal data for compounds **1**, **2**, and **3** is given in Table 1. Final atomic coordinates are displayed in Table 2, and selected bond distances and angles are in Table 3.

Table 3. Selected Bond Distances and Angles for $NaLa(SO_4)_2 \cdot H_2O$ (Regular Characters), $NaNd(SO_4)_2 \cdot H_2O$ (Bold), and $NaGd(SO_4)_2 \cdot H_2O$ (Italic)[a−f]

Bond Distances (Å) for 1, **2**, and *3*			
M(1)−O(1)	2.590(4)	S(1)−O(1)	1.479(5)
	2.547(3)		**1.472(4)**
	2.506(7)	*S(1)−O(1)*[d]	*1.494(7)*
M(1)−O(2)	2.599(4)	S(1)−O(2)	1.486(4)
	2.531(4)		**1.480(4)**
	2.488(7)		*1.487(7)*
M(1)−O(3)	2.508(5)	S(1)−O(3)[a]	1.474(5)
	2.461(4)		**1.470(4)**
	2.405(7)	*S(1)−O(3)*[e]	*1.475(7)*
M(1)−O(4)	2.510(5)	S(1)−O(4)[b]	1.461(5)
	2.460(5)		**1.463(4)**
	2.398(8)	*S(1)−O(4)*[f]	*1.479(8)*
M(1)−O(5)	2.56(1)		
	2.492(8)		
	2.47(1)		

Bond Angles (°) for 1, **2**, and *3*			
O(1)−S(1)−O(2)	105.9(2)	O(2)−S(1)−O(3)[a]	109.7(3)
	105.5(2)		**109.6(2)**
O(1)[d]*−S(1)−O(2)*	*105.5(4)*	*O(2)−S(1)−O(3)*[e]	*110.2(4)*
O(1)−S(1)−O(3)[a]	111.4(3)	O(2)−S(1)−O(4)[b]	110.9(3)
	111.4(2)		**110.8(2)**
O(1)[d]*−S(1)−O(3)*[e]	*111.7(5)*	*O(2)−S(1)−O(4)*[f]	*110.4(5)*
O(1)−S(1)−O(4)[b]	111.4(3)	O(3)[a]−S(1)−O(4)[b]	107.5(3)
	111.9(2)		**107.7(2)**
O(1)[d]*−S(1)−O(4)*[f]	*111.0(4)*	*O(3)*[e]*−S(1)−O(4)*[f]	*108.1(4)*

[a−f] Symmetry transformations used to generate equivalent atoms: $a = -x + y + 1, -x + 1, z - {}^{1}/_{3}$; $b = -x + y, -x + 1, z - {}^{1}/_{3}$; $c = y, x, -z + 2$; $d = y, x, -z$; $e = = -y + 1, x - y + 1, z - {}^{1}/_{3}$; $f = -y + 1, x - y, z - {}^{1}/_{3}$.

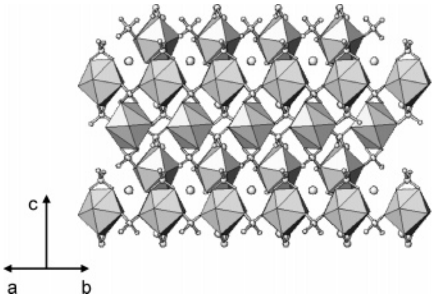

Figure 1. View of the $NaM(SO_4)_2 \cdot H_2O$ structure along [110], showing the MO_9 polyhedra linked by the SO_4 groups.

As was mentioned before, the rare-earth compounds $NaM(SO_4)_2 \cdot H_2O$ were known to be isostructural, as shown by the powder diffraction results. Indeed, we found that $NaNd(SO_4)_2 \cdot H_2O$ shows the same structural type as $NaLa(SO_4)_2 \cdot H_2O$,[4] and $NaGd(SO_4)_2 \cdot H_2O$ is isostructural with the second enantiomorph of $NaCe(SO_4)_2 \cdot H_2O$.[7] In the structures of compounds **1**, **2**, and **3**, there are nine-coordinated M^{3+} centers and eight-coodinated Na^+ ions. The rare-earth polyhedra MO_9 are distorted tricapped trigonal prisms, joined among them by the SO_4 tetrahedra (Figure 1). The distortion of the coordination polyhedra is understandable due to the existence of different ligands surrounding the metallic center (H_2O and SO_4), and the different bonding modes the sulfate group exhibits. In the three compounds, the SO_4 polyhedra show similar bond distances and angle values: S−O distances range from 1.461(5) to 1.486(4) Å in the lanthanum sulfate, from 1.463(4) to 1.480(4) Å in the neodymium derivative, and from 1.475(7) to 1.494(7) Å in the gadolinium compound. The O−S−O angles are between 105.9(2) and 111.4(2)° in $NaLa(SO_4)_2 \cdot H_2O$, between 105.5(2) and 111.9(2)° in $NaNd(SO_4)_2 \cdot H_2O$, and between 105.5(4) and 111.7(7)° in $NaGd(SO_4)_2 \cdot H_2O$.

Each rare-earth atom is coordinated to one oxygen (O5) from the water molecule (M−O5 distance 2.56(1), 2.492(8), and 2.47(1) Å for La, Nd, and Gd sulfates, respectively) and eight oxygen atoms from six SO_4 groups (four of them

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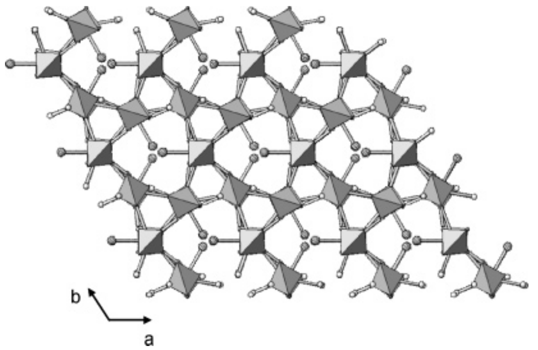


Figure 2. View of the $NaM(SO_4)_2\cdot H_2O$ structure along [001], showing the SO_4 tetrahedra and the coordinated water molecules inside the tunnels formed by the framework.

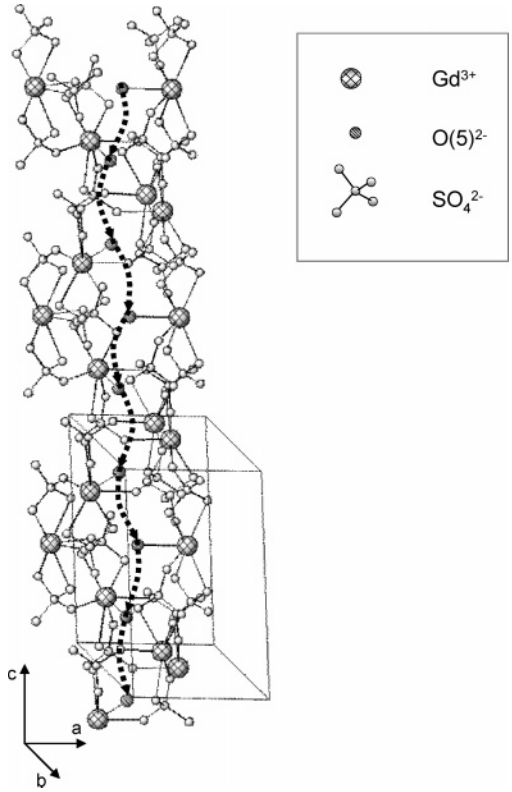


Figure 3. The coordinated water molecules are placed in a helical shape following the screw axis parallel to *c*. In this figure, we can see the 3_2 axis in the structure of $NaGd(SO_4)\cdot H_2O$.

contributing one oxygen atom and two of them providing two). The M−O distances range from 2.599(4) to 2.508(5) Å for M = La, from 2.547(3) to 2.508(5) Å for M = Nd, and from 2.506(7) to 2.398(8) Å for M = Gd.

The water molecules are placed into a helical fashion corresponding to the 3_1 (in **1** and **2**) or 3_2 (in **3**) axis (Figures 2 and 3). Each SO_4 group is bonded to three metallic centers, acting as chelating and bridging simultaneously: two oxygen atoms are connected to the same M^{3+} and the remaining two link other two different metal atoms. As can be seen in Table 4, there are asymmetric bifurcated hydrogen bonds that connect the coordinated water molecules (O5 acts as donor atom) to the framework, involving the sulfate oxygen atoms O2 and O3.

Table 4. Hydrogen Bond Distances (Å) and Angles (°) for $NaLa(SO_4)_2\cdot H_2O$ (Regular Characters), $NaNd(SO_4)_2\cdot H_2O$ (Bold), and $NaGd(SO_4)_2\cdot H_2O$ (Italic)

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
O(5)−H···O(2)[a]	1.1(1)	2.1(1)	3.228(5)	167(10)
	0.89(7)	**2.36(7)**	**3.236(4)**	**171(8)**
O(5)−H···O(2)[b]	*1.0(1)*	*2.3(1)*	*3.214(8)*	*171(12)*
O(5)−H···O(3)[c]	1.1(1)	2.3(1)	2.945(9)	118(7)
	0.89(7)	**2.40(7)**	**2.966(8)**	**122(6)**
	1.0(1)	*2.3(1)*	*2.94(1)*	*122(11)*

[a−c] Symmetry transformations used to generate equivalent atoms: $a = -y + 2, x - y + 1, z + ^1/_3$; $b = x + 1, y + 1, z$; $c = -x + y + 1, -x + 2, z + ^1/_3$.

It is a remarkable fact that the size of the A^+ ion seems to play an important role in the number of water molecules present in the structure of the $AM(SO_4)_2\cdot nH_2O$ compounds. They are either monohydrates,[4−13] dihydrates,[14−16] or tetrahydrates,[17−25] depending mainly on the type of A^+ cation. For small A^+ ions such as Na^+, the monohydrates become dominating and tetrahydrates are only found for bigger monovalent ions Cs^+, NH_4^+, and Rb^+.

Among the monohydrates, we can find two groups of isostructural compounds. One of them is the $AM(SO_4)_2\cdot H_2O$ sulfates with large A^+ ions such as K^+ or Rb^+: they crystallize in the monoclinic $P2_1/c$ space group.[11−13] The other group is formed by the Na^+ derivatives; these are trigonal and have either $P3_121$ or $P3_221$ symmetry.[4−7] Replacement of Na^+ for Ag^+ is possible in $NaCe(SO_4)_2\cdot H_2O$ without structural changes,[6] while the incorporation of smaller Li^+ ions leads to a completely different layered structure.[8]

However, it seems quite plausible that the combination of the A^+ ion size and the rare-earth atom is not the only factor responsible for the resulting crystal structure and the number of water molecules present in the compound. For instance, in the case of lanthanum and neodymium hydrated ternary sulfates, the influence of the A^+ size is clear. Thus, we find the monohydrates $NaLa(SO_4)_2\cdot H_2O$ and $NaNd(SO_4)_2\cdot H_2O$ with a small A^+ ion, and the layered tetrahydrates $(NH_4)La(SO_4)_2\cdot 4H_2O$, $(NH_4)Nd(SO_4)_2\cdot 4H_2O$, $RbLa(SO_4)_2\cdot 4H_2O$, $RbNd(SO_4)_2\cdot 4H_2O$, and $CsLa(SO_4)_2\cdot 4H_2O$ with larger A^+ ions. However, in the case of gadolinium compounds, the small Na^+ ion yields monohydrated trigonal $P3_221$ crystal structures, but larger ions as Rb^+ give rise to a 3D monoclinic $P2_1/c$ monohydrate, and also a layered tetrahydrate $RbGd(SO_4)_2\cdot 4H_2O$. This behavior is also found in Ce sulfates: a trigonal monohydrate with Na^+ is reported, but with a larger Rb^+ ion, both the 3D monoclinic monohydrate and layered tetrahydrate are described.[25] Given the fact that the synthesis of $RbCe(SO_4)_2\cdot 4H_2O$ yielded also $RbCe(SO_4)_2\cdot H_2O$, it is not clear at the moment which factors are responsible for the formation of sulfates with the same lanthanide center and A^+ ion, but different number of water molecules and crystal structures.

Catalytic Activity. The three compounds **1**, **2**, and **3** were tested for catalytic properties in the oxidation of sulfides to prove their effect in redox reactions. Two substrates were used with different steric volumes to investigate the influence of the geometrical factors.

Two thioethers, methylphenylsulfide and (2-ethylbutyl)phenylsulfide, were used as model substrates with H_2O_2, as the oxygen source, always in excess of the amount of substrate. The reactions were carried out at 40 °C, as higher

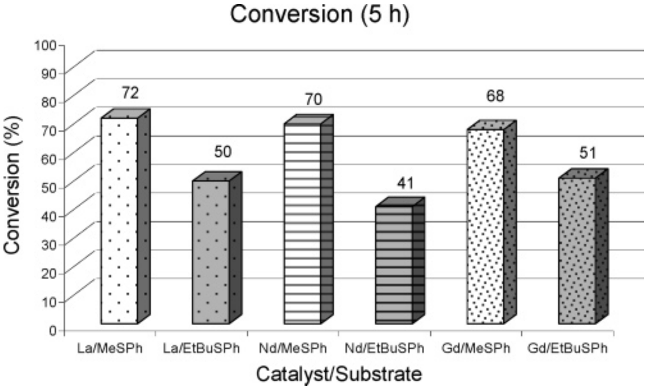


Figure 4. Activity of compounds $NaLa(SO_4)_2{\cdot}H_2O$, $NaNd(SO_4)_2{\cdot}H_2O$, and $NaGd(SO_4)_2{\cdot}H_2O$ in the oxidation of sulfides [MeSPh = methylphenylsulfide; EtBuSPh = (2-ethylbutyl)phenylsulfide].

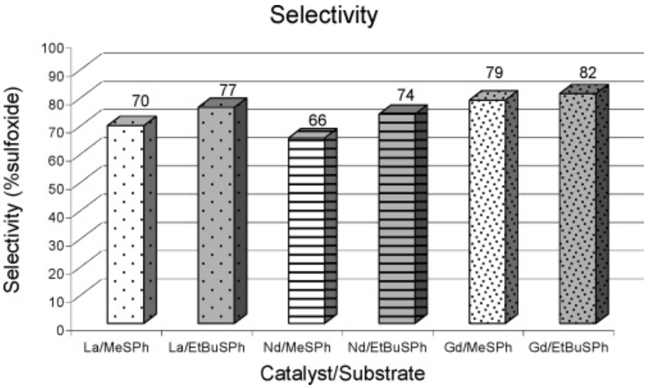
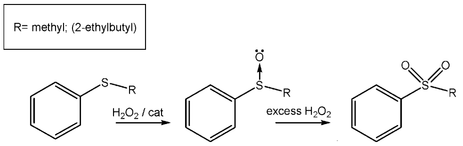


Figure 5. Selectivity to sulfoxide of compounds $NaLa(SO_4)_2{\cdot}H_2O$, $NaNd(SO_4)_2{\cdot}H_2O$, and $NaGd(SO_4)_2{\cdot}H_2O$ in the oxidation of sulfides [MeSPh = methylphenylsulfide; EtBuSPh = (2-ethylbutyl)phenylsulfide], at 60% conversion.

Scheme 1. Oxidation of Alkylphenyl Sulfides



reaction temperatures lead to a dramatic decrease in the selectivity to sulfoxide. The outcome of the reaction was followed by GC to identify the products. The results in activity and selectivity are summarized in Figures 4 and 5. Blank experiments were carried out, with both sulfides and excess of oxidant, under identical test conditions, and conversions lower than 3% after 2 h were obtained, even at higher temperatures. The employment of 1.0 equiv instead of 1.5 equiv of H_2O_2, and its controlled addition, allowed a significant improvement of the chemoselectivity of the process, and sulfoxide was obtained as the only product. The materials are extremely efficient and catalyze the selective sulfoxide formation under mild conditions. Total conversion was reached with the catalysts after 24 h of reaction. However, at high conversion values (>90%), the oxidation does not stop at the sulfoxide level and proceeds, yielding overoxidized products such as sulfone (Scheme 1). The selectivity analysis shows that the sulfoxide is a primary and unstable product, while the corresponding sulfone appears as a secondary and stable product to high conversion. The best values of selectivity are found in the oxidation of the bulky substrate (Figure 5): it is a known fact that usually slower reactivity provides higher selectivity. Total conversion to the corresponding sulfone was obtained using 2.5 equiv of oxidant agent, at 40 °C. A logical slight decreasing rate is observed when a bulky substrate is oxidized, as (2-ethylbutyl)phenylsulfide. If we compare the catalytic results of $NaM(SO_4)_2{\cdot}H_2O$ sulfates with the previously studied sulfate $Nd(SO_4)_2{\cdot}NH_4$,[1] we find that with use of $Nd(SO_4)_2{\cdot}NH_4$ as a catalyst, the sulfide oxidation reaction proceeds faster than it does with $NaM(SO_4)_2{\cdot}H_2O$; however, the selectivity is lower. The shorter reaction times obtained using this sulfate can be explained by the easier availability of the metallic centers in this compound due to its layered structure.

A remarkable feature of the three materials, $NaLa(SO_4)_2{\cdot}H_2O$, $NaNd(SO_4)_2{\cdot}H_2O$, and $NaGd(SO_4)_2{\cdot}H_2O$, is their behavior as heterogeneous catalysts. The main advantages of heterogeneous catalysis over its homogeneous counterpart are the ease of recovery and recycling of the catalyst and the easier working procedure, which allows the removal of the catalysts from the reaction media through a simple filtration. The lifetime of the obtained heterogeneous catalysts was examined by using them in several reaction cycles. Before reusing them, the solids were separated from the reaction medium by filtration and washed with dichloromethane. The catalysts could be reused at least four times without neither loss of activity nor selectivity with catalyst loading as low as 1.5 mol %. The slight decrease observed for the consecutive runs is due to the small amount of catalytic material lost by filtration. While the oxidation of the sulfide continued as the catalyst was present, there was no further significant conversion when the catalyst was removed from the reaction medium. The structures of the catalysts remain unchanged after the reaction, as we confirmed by powder X-ray analysis.

The nature of the intermediate catalytic species is not yet clear, and no reports have been found in the literature concerning the elucidation of the nature of complexes between rare-earth derivatives and hydrogen peroxide, although lanthanide metals combined with H_2O_2 are known to accelerate greatly the hydrolysis of phosphates in aqueous systems.[36] These data may suggest that a peroxo derivative (M−O−O) can be formed and be the species responsible for the reaction.[37] The kinetic profiles of the three compounds in both reactions (Figure 6) show that they have similar behavior: there is almost no difference in yield for **1**, **2**, and **3** in the oxidation of sulfides, probably due to their similar ability to increase the coordination for the three metallic centers. Our hypothesis is that the performance of these materials as catalysts is related to the ability of the metallic centers in them to accommodate another coordination position in order to form the peroxo derivative. This hypothesis is supported by previous results obtained in our research group with organo-inorganic 3D polymeric materials in the oxidation of sulfides:[38] metallic centers such as scandium, which increase their coordination number less

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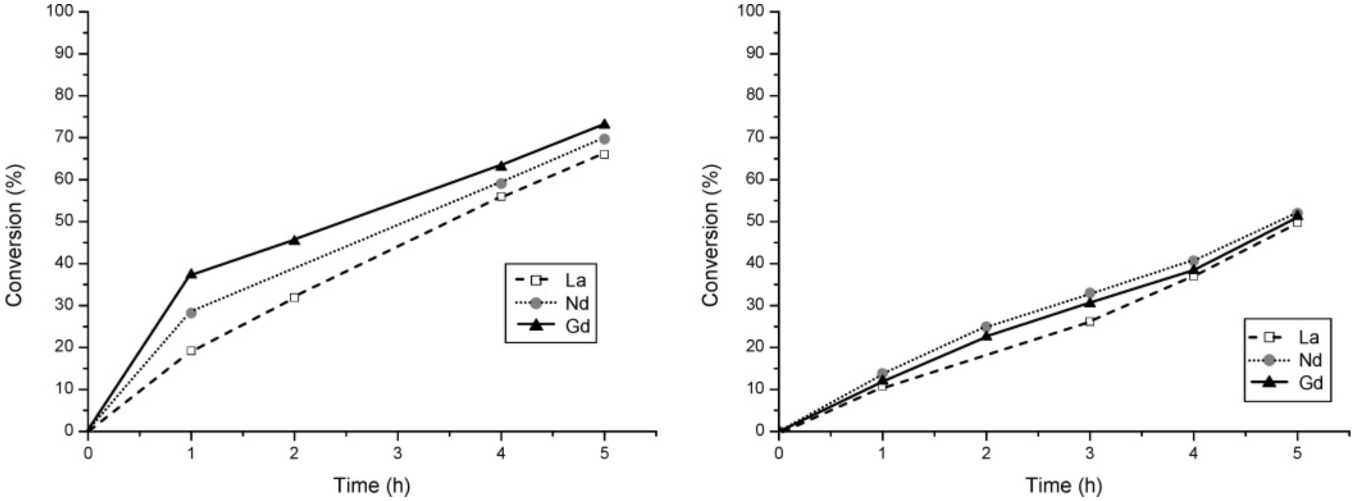

Figure 6. Kinetic profile of the oxidation of methylphenylsulfide (left) and (2-ethylbutyl)phenylsulfide (right), using as catalysts $NaM(SO_4)_2{\cdot}H_2O$ M = La, Nd, and Gd.

easily, yield poorer catalysis results compared to lanthanum or yttrium. Another argument in favor of this hypothesis is the excellent behavior as a catalyst of $Nd(SO_4)_2{\cdot}NH_4$[1]; although the structure of this sulfate is not analogous to the $NaM(SO_4)_2{\cdot}H_2O$ sulfates, its catalytic activity is also noteworthy, possibly due to the existence of available 9-coordinated neodymium centers, which can easily form the needed intermediate 10-coordinated species. In fact, the layered structure of $Nd(SO_4)_2{\cdot}NH_4$ contributes to further improve the availability of the metallic centers, leading to a better performance of this material as a catalyst.

In summary, we can conclude that these rare-earth based catalytic systems induce efficiently the oxidation of aliphatic sulfides with 30% hydrogen peroxide and **1**, **2**, or **3** as catalysts in acetonitrile, giving good yields. The systems are mild, simple, clean, and cheap methods for the oxidation of sulfides to sulfoxides.

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Supporting Information Available: Crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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