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# Epoxidation of Olefins Catalyzed by Sulfate-based Supramolecular Ion Pairs

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**Abstract:** The development of inexpensive and effective catalysts for the epoxidation of olefins to epoxides, key commodities for the chemical industry, is a continuing challenge. In this context, we present a supramolecular solution with the development of new host-guest assemblies of sulfate ions and amidoammonium receptor cations that, for the first time, are shown to act as catalysts for olefin epoxidation by hydrogen peroxide under biphasic conditions. Analysis of the reaction mechanism shows that reactive and oxidizing peroxymonosulfate is formed in the organic phase. Furthermore, a variety of readily available precursors may be used to form the guest supramolecular cations, so enabling large scale synthesis of the catalysts while maintaining catalytic control and effectiveness.

## Introduction

The epoxidation of olefins with molecular catalysts in homogeneous phase is an important field of research, as epoxides span a broad range of applications, such as intermediates for the synthesis of value-added (chiral) fine chemicals.<sup>[1]</sup> The catalyst spectrum encompasses high-performance complexes of Group 4 to 7<sup>[2]</sup> as well as metal-free organocatalysts.<sup>[3]</sup> With this being said, in molecular epoxidation catalysis the fate of the catalyst is often not of interest, and it is being discarded in order to isolate the valued-added product. The growing need to deal with our resources considerately and in a sustainable way raises the question how to make homogeneous epoxidation reactions more viable in terms of inexpensive and recyclable catalysts. Furthermore, the choice of oxidant mostly depends on the compatibility with the catalyst and not on the criteria of green chemistry.<sup>[4]</sup> For this reason, much research has been devoted to supramolecular concepts to perform biphasic epoxidations using hydrogen peroxide as green oxidant, either allowing or preventing phase transfer of the catalyst to the substrate, depending on the requirements.<sup>[5]</sup> While in most biphasic liquid-liquid epoxidations both the substrate/product and the catalyst are in the same phase, there are far less examples for epoxidations in water. Recently, we have shown that surface-

active ionic liquids containing catalytically active  $[\text{MO}_4]^{n-}$  anions ( $M = \text{Re}, \text{W}; n = 1, 2$ ) form micelles in aq.  $\text{H}_2\text{O}_2$ , which are capable of solubilizing a hydrophobic olefin in water, thereby performing the catalysis in the aqueous phase; this feature allows for a separation of the product and catalyst phases.<sup>[6,7]</sup> The rather unusual mode of  $\text{H}_2\text{O}_2$  activation by the perrhenate anion via hydrogen bonding<sup>[8]</sup> raised the question, whether other, metal-free element-oxo anions could be used for the epoxidation of hydrophobic, unfunctionalized olefins in micellar environments via a similar mechanism. It should be noted that metal-free epoxidation catalysts are not systematically investigated in the epoxidation of (industrially relevant) hydrocarbon-only olefins. Studies of the catalytically active nitrate anion have indeed revealed that  $[\text{NO}_3]^-$  activates  $\text{H}_2\text{O}_2$  analogously to perrhenate, albeit with a relatively poor catalytic activity and selectivity,<sup>[9]</sup> which is why the focus turned to the sulfate anion. It is well-known that in aq.  $\text{H}_2\text{O}_2$  solution  $[\text{SO}_4]^{2-}$  reacts to form the peroxymonosulfate anion  $[\text{HSO}_5]^-$ , which is highly reactive towards the unselective (radical) oxidation of C–H and C–C bonds, thus rendering a catalytic reaction unfeasible.<sup>[10]</sup> Hence, it is not surprising that in the literature sulfate itself has not been used as a selective epoxidation catalyst in water. The  $[\text{HSO}_5]^-$  anion is, however, a well-known oxidant known as Oxone,  $\text{K}[\text{HSO}_5]$  (stabilized by  $\text{KHSO}_4$  and  $\text{K}_2\text{SO}_4$ ), which is widely applied as a stoichiometric oxidant in metal-free Shi-type epoxidations with ketones as catalysts in organic phase.<sup>[3c,11,12]</sup> and even in water.<sup>[13,14]</sup> In these cases, the byproduct sulfate cannot be recycled into the  $[\text{HSO}_5]^-$  anion in a catalytic fashion, i.e., sulfate is a stoichiometric waste product of Oxone. This shortcoming, together with our results in the application of element-oxo anions in supramolecular epoxidations has led us to study the potential of the sulfate anion as catalyst for the epoxidation of olefins in organic phase using aq.  $\text{H}_2\text{O}_2$  as oxidant.

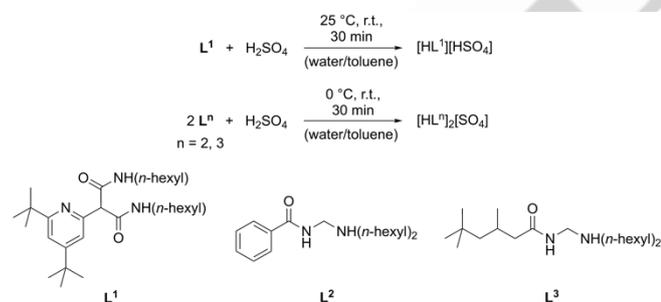
The transfer of water-soluble oxo anions into an organic phase is a recurring theme in hydrometallurgical separation chemistry. Romański and co-workers reported the selective transfer of sulfate ions from water into chloroform by using a squaramide-based receptor.<sup>[15]</sup> Our approach leads back to the work of Tasker, Love, and co-workers who developed

amidoammonium receptors for the extraction of metalates from aqueous acid solutions into an organic phase via supramolecular hydrogen bonding interactions between receptor and anion.<sup>[16,17]</sup> We exploited this concept for the solubilization of perrhenate anions into the substrate/toluene phase, forming so-called supramolecular ion pairs (SIPs) which are highly active catalysts in the epoxidation of olefins.<sup>[18]</sup> Application of these principles to the transfer of the in-situ generated  $[\text{HSO}_5]^-$  into the substrate phase by a SIP should prevent the non-desired over-oxidation of the substrate due to the catalytic presence of oxidant as part of the supramolecular assembly. Hence, in this study, we report on the synthesis, characterization and catalytic performance of sulfate-based SIP assemblies for the epoxidation of olefins in a biphasic liquid/liquid system. Variation of the receptor motif in order to change polarity and steric demand of the catalyst allows for a better understanding of the crucial factors for an efficient and selective metal-free catalyst.

## Results and Discussion

### Synthesis and Characterization of the Supramolecular Ion Pairs (SIPs)

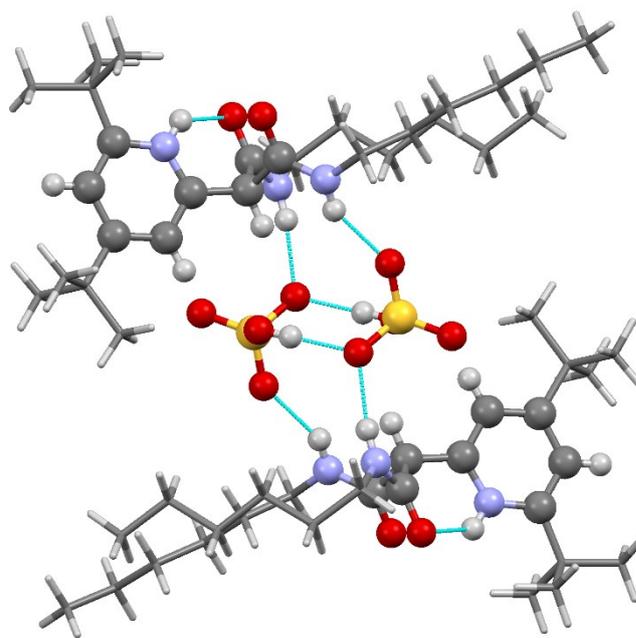
The sulfate-based ion pairs shown in Scheme 1 were prepared by extraction of diluted sulfuric acid (1M solution) to the toluene phase with the previously reported organic receptor molecules  $\text{L}^1$ – $\text{L}^3$ <sup>[17]</sup> and studied the ion pair formation with equimolar amounts of aqueous sulfuric acid. The herein investigated structural motifs were chosen as promising candidates with different polarities and steric demand in order to evaluate these parameters in the catalytic performance in olefin epoxidation.



**Scheme 1.** Synthesis of the amidoammonium sulfate SIPs from the neutral receptor compounds  $\text{L}^1$ – $\text{L}^3$  and sulfuric acid.

After phase separation and toluene evaporation under reduced pressure, the three SIPs were isolated as colorless solid for  $\text{L}^1$  or pale-yellow oils in the case of  $\text{L}^2$  and  $\text{L}^3$ , respectively. All three SIPs are highly soluble in toluene and other common organic solvents.

Slow evaporation of toluene from a solution of  $[\text{HL}^1][\text{HSO}_4]$  afforded crystals suitable for single crystal X-ray diffraction. The solid-state structure reveals that only one deprotonation of sulfuric acid via the basic pyridine-N atom has taken place, leading to hydrogensulfate anions, and a ratio  $[\text{HL}^1]:[\text{HSO}_4]$  of 1:1. Two H-bonded  $[\text{HSO}_4]^-$  anions are interacting with two protonated



**Figure 1.** The X-ray single crystal structure of  $[\text{HL}^1][\text{HSO}_4]$  illustrating the hydrogen bonding interactions. The tert-butyl and n-hexyl substituents are drawn as wireframes for clarity.

receptor molecules  $[\text{HL}^1]^+$  (Figure 1 **Error! Reference source not found.**), which is similar to the reported perrhenate-SIP.<sup>[18]</sup> The structure of  $[\text{HL}^1][\text{HSO}_4]$  can be regarded as an organic capsule formed by the hydrophobic parts of the receptor containing the polar hydrogensulfate ions connecting the receptor molecules by H-bonds, enabling a high solubility in hydrocarbon solvents. The pyridinium proton forms a bifurcated hydrogen bond to the two amide oxygen atoms as part of two, six-membered, proton-chelate rings. This pre-organizes the receptor such that an array of classical N–H and non-classical C–H hydrogen bonds are formed between the receptors and the  $[\text{HSO}_4]^-$  anions, along with intermolecular hydrogen bonding between the two hydrogensulfate anions.

The structure of  $[\text{HL}^1][\text{HSO}_4]$  was further investigated by  $^1\text{H-NMR}$  spectroscopy, which confirms that the receptor cation structure remains fully intact and is protonated (see the Supporting Information, SI, Figure S4). This finding is corroborated by the elemental analysis results, supporting the formal composition  $[\text{HL}^1][\text{HSO}_4]$ .

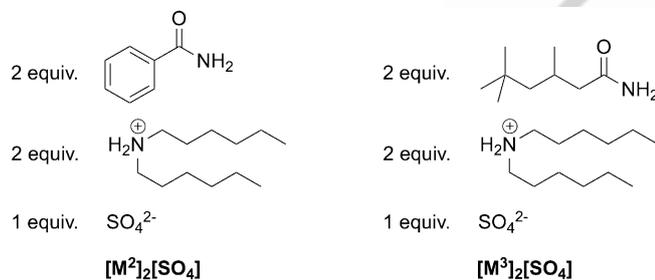
In the case of the reaction of the receptors  $\text{L}^2$  and  $\text{L}^3$  with  $\text{H}_2\text{SO}_4$  the elemental analysis suggests a receptor:sulfate ratio of 2:1, hinting to a full deprotonation of sulfuric acid and hence the formal composition  $[\text{HL}^n]_2[\text{SO}_4]$  ( $n = 2, 3$ ) (see the SI). Accordingly, the  $^1\text{H-NMR}$  spectra of these two SIPs reveal that the dihexylamine moiety is expectedly protonated both in  $\text{L}^2$  and  $\text{L}^3$ . However, the spectra also clearly show that the receptor cation is partially decomposed (SI, Figures S5 and S6). First, signals attributed to dihexylammonium ions at 10.18 ppm in the case of  $[\text{HL}^2]_2[\text{SO}_4]$  and 11.18 ppm for  $[\text{HL}^3]_2[\text{SO}_4]$  appear, and free amide ( $-\text{CONH}_2$ ) protons appear at around 6 ppm in both cases. Second, the signal of the methylene group bridging the amide and amino moieties in  $\text{L}^2$  and  $\text{L}^3$  decreases in intensity.

These observations point to an acid-induced fragmentation of the receptors into the amide, the dihexylammonium cation, and

formaldehyde during the reaction of the neutral receptors with sulfuric acid. In the case of the SIP  $[\text{HL}^n]_2[\text{SO}_4]$ , the ortho-ring protons of the benzamide moiety (SI, Figure S5) can serve as probes for the degree of decomposition of the  $\text{HL}^2$  cation to benzamide and dihexylammonium sulfate (DHA). While the signal of these protons in intact  $[\text{HL}^2]_2[\text{SO}_4]$  arises at 8.03 ppm, that of free benzamide appears in the same spectrum at 7.80 ppm, with a proton ratio of roughly 2.5:1. From this, it can be deduced that the decomposition degree of the intact SIP is around 39%. For the SIP  $[\text{HL}^3]_2[\text{SO}_4]$  the  $^1\text{H-NMR}$  spectrum (SI, Figure S6) shows a more complex pattern with overlapping resonances, suggesting that more side reactions occur than the receptor degradation which is leading 3,3,5-trihexylamide and DHA, prohibiting an estimation of the degree of SIP decomposition.

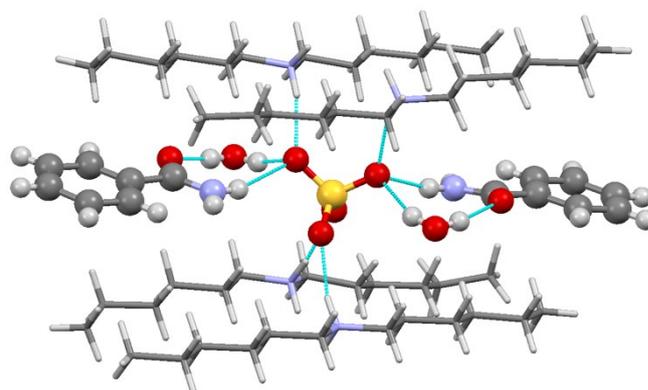
The degradation of  $\text{L}^2$  and  $\text{L}^3$  was observed before in the synthesis of the analogous perchlorate SIPs.<sup>[18]</sup> In this case, it is shown that an in-situ formed mixture of an amide, dihexylammonium cations and an element-oxo anion still forms a catalytically active supramolecular ion pair which is soluble in organic solvents. As such, the products of the reaction of  $\text{L}^2$  and  $\text{L}^3$  with  $\text{H}_2\text{SO}_4$ , denoted as  $[\text{HL}^2]_2[\text{SO}_4]$  and  $[\text{HL}^3]_2[\text{SO}_4]$ , can be considered as SIPs and consequently, we have tested these compounds in their catalytic performance.

The fact that the SIP cations can break up into single components and still form a supramolecular network has led us to investigate if such a SIP could directly be synthesized from the very cheap starting materials organic amide/dihexylammonium sulfate, and thus avoid synthesizing the receptor. The mixtures which were used for synthesizing the SIPs are shown in Figure 3 and the "mixture-SIPs" obtained by this route are denoted as  $[\text{M}^n]_2[\text{SO}_4]$  ( $n = 2, 3$ ).



**Figure 3.** Composition of the mixtures which in situ form the SIPs  $[\text{M}^n]_2[\text{SO}_4]$  ( $n = 2, 3$ ).

The amide/dihexylammonium sulfate combination is expected to form the respective SIP in situ with the lack of the bridging methylene group not influencing the SIP assembly. In a first test, the precursors benzamide (BA) and dihexylammonium sulfate (DHA) (molar ratio 2:1) were dissolved in a water/toluene mixture upon heating to 80 °C and the separated toluene phase was slowly evaporated at room temperature. The formed crystals were investigated by single crystal X-ray diffraction which shows that, in the solid state, the precursors form a supramolecular H-bond network of the composition  $[\text{BA}/\text{DHA}/\text{H}_2\text{O}]_m$  with the anticipated SIP amide/ammonium/sulfate ratio 2:2:1 (Figure 4). This results in an organic capsule formed by layers of dihexylammonium cations binding to the inter-layer sulfate anion. Furthermore, the benzamide protons bind to the sulfate dianion via H-bonds, further stabilizing the supramolecular SIP structure.



**Figure 4.** Representation of the X-ray single crystal structure of the mixture-SIP  $[\text{M}^2]_2[\text{SO}_4]$ . The n-hexyl chains are drawn as wireframes for clarity. Note that the four dihexylammonium cations are each shared with the adjacent SIP units.

It is also noteworthy that two molecules of water per  $[\text{M}^2]_2[\text{SO}_4]$  SIP unit are incorporated in the structure, which is in good agreement with the elemental analysis of the constitutional analogue SIP  $[\text{HL}^2]_2[\text{SO}_4]$ , which also contains 1.5 equiv. of water per SIP.

The  $^1\text{H-NMR}$  spectra of the new "mixture-SIPs" (SI, Figures S7 and S8) show that the signals of the starting materials are all present, yet somewhat shifted compared to the educts, most presumably giving rise to the formation of the SIP via H-bonds, which influence the shift.

### Mechanism of the Formation of the Sulfate-SIPs

To gain insights into the formation of the SIPs  $[\text{M}^n]_2[\text{SO}_4]$  in solution, the sizes of the SIP assemblies of benzamide or 3,3,5-trimethylhexanamide and dihexylammonium sulfate,  $[\text{M}^2]_2[\text{SO}_4]$  and  $[\text{M}^3]_2[\text{SO}_4]$ , in solution were investigated by  $^1\text{H}$  nuclear magnetic resonance diffusion ordered spectroscopy (NMR-DOSY) and dynamic light scattering (DLS). The results are summarized in Table 1. For the first method, the single components and the mixtures thereof were dissolved in benzene- $d_6$  and stirred at 80 °C for 1 h and then analyzed by NMR-DOSY, giving access to the diffusion coefficient of the species in solution, which correlates with the hydrodynamic radii of the solvated aggregates according to *Stokes-Einstein* equation (SI, Figures S12–S14).

The analysis of neat benzamide or 3,3,5-trimethylhexanamide gives rather small hydrodynamic radii of 2.79 and 2.93 Å, respectively. In contrast, a dihexylammonium sulfate solution presents significantly larger assemblies with radii of 126 Å, suggesting the formation of large supramolecular structures such as inverse micelles in the benzene solution. Remarkably, mixing the amides and dihexylammonium sulfate in a 2:1 ratio, leads to assemblies of the size of 9.0 and 9.7 Å for  $[\text{M}^2]_2[\text{SO}_4]$  and  $[\text{M}^3]_2[\text{SO}_4]$ , respectively, formed along with aggregates of a radius of 17.1 Å. For comparison, from the X-ray single crystal structure, the organic receptor  $\text{L}^1$  describes a radius of 6.7 Å, which increases slightly to 9.0 Å upon protonation to the SIP  $[\text{HL}^1][\text{HSO}_4]$ , supporting that  $\text{L}^1$  exists as a dimer in solution and that a dimeric SIP structure of the crystallographic data correlates well to the structure in solution.

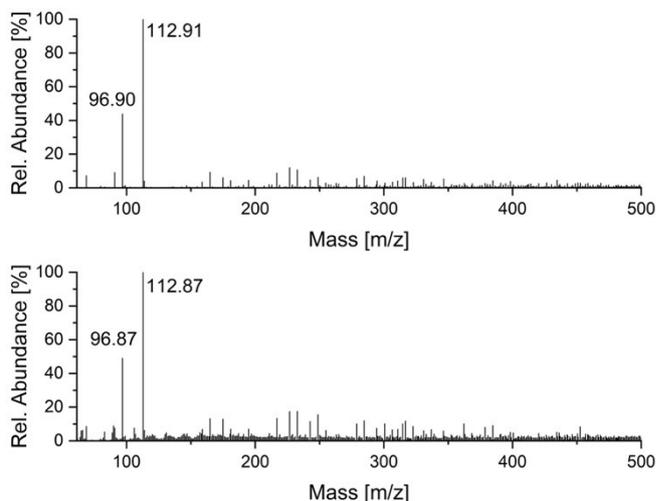
Additional DLS measurements support the NMR-DOSY data for SIP formation in toluene solution. The samples were prepared similarly to the NMR-DOSY approach but using toluene as solvent and measured before and after heating to 80 °C to study the temperature dependency of assembly formation. While the hydrodynamic radius of  $[M^2]_2[SO_4]$  decreases from 19.8 to 12.9 Å after heating, which is in agreement with the NMR-DOSY analysis, the size of  $[M^3]_2[SO_4]$  decreases slightly from 21.4 to 18.2 Å (SI, Figures S15 and S16), suggesting a preferred formation of the larger dynamic assembly as shown by NMR-DOSY (17.1 Å). This formation of a SIP dimer can be explained by the favored assembly of two sulfate anions with four amide and two dihexylammonium cations. This is likely triggered by the steric demand of the trimethylpentyl substituent on the amide, compared with the flat phenyl group, allowing for a larger ionic cavity, in which two sulfate anions fit. In comparison, the DLS hydrodynamic radius of the SIP  $[HL^1][HSO_4]$  remains more or less constant at 6.4 and 5.8 Å before and after heating and appears slightly smaller in toluene than in benzene- $d_6$  (SI, Figure S17).

**Table 1.** Radii of the three SIPs analyzed by various methods.

SIP	DOSY [Å]	DLS [Å]	SC-XRD [Å]
$[HL^1][HSO_4]$	8.9	6.4	9.1
$[M^2]_2[SO_4]$	9.0 and 17.1	12.9	8.0
$[M^3]_2[SO_4]$	9.7 and 17.1	18.2	n.a.
$[DHA]_2[SO_4]$	126	135	n.a.

### Reactivity of Sulfate-SIPs with Hydrogen Peroxide

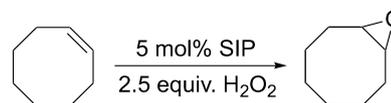
The elemental analysis data of the synthesized SIPs, as well as the X-ray single crystal structure of the SIPs  $[HL^1][HSO_4]$  and  $[M^n]_2[SO_4]$  show that the SIPs are able to incorporate water molecules in the SIP structure, despite being highly soluble in an organic phase and not in water. This suggests that phase transfer of hydrogen peroxide for epoxidations in the organic phase should also be possible. Therefore, we investigated the formation of a possible persulfate species by mass spectrometry. In an exemplary experiment, the neat SIP  $[M^2]_2[SO_4]$  was stirred in 50 wt.% aqueous hydrogen peroxide at 80 °C for 5 h and then extracted with toluene. After evaporation of toluene in vacuo, the SIP was redissolved in acetonitrile and analyzed by negative-ion electrospray ionization mass spectrometry (ESI-MS). The formation of peroxymonosulfate is verified by detection of a major peak at  $m/z$  112.9, corresponding to  $[HSO_5]^-$ , along with another peak at  $m/z$  96.9, which is attributable to  $[HSO_4]^-$  (Figure 5, top spectrum). The ratio of monoanionic hydrogensulfate ( $m/z$  97) to hydrogenpersulfate ( $m/z$  113) does not change when the SIP is treated with hydrogen peroxide for just 5 min (Figure 5, bottom spectrum). Natural abundance  $^{33}S$ -NMR studies to further investigate the temperature dependency and the kinetics of the formation of persulfate species under catalysis conditions were not successful due to the quadrupolar moment of the  $^{33}S$  nucleus leading to broad peaks and a potential full overlap of the signals due to the small chemical shift difference between the two sulfate species (0 ppm and -23 ppm for sulfate and persulfate, respectively).<sup>[19]</sup> From the ESI-MS results it is evident that the peroxymonosulfate anion is formed upon contact with  $H_2O_2$  in the biphasic SIP system and transferred to the substrate phase, which are the two essential premises for examining the catalytic activity of sulfate-based SIPs.



**Figure 5.** Negative mode ESI-MS spectra of a mixture of  $[M^2]_2[SO_4]$  and hydrogen peroxide after 5 h at 80 °C (top spectrum) and after 5 min at room temperature (bottom).

### Sulfate-SIPs as Catalysts for the Epoxidation of Olefins

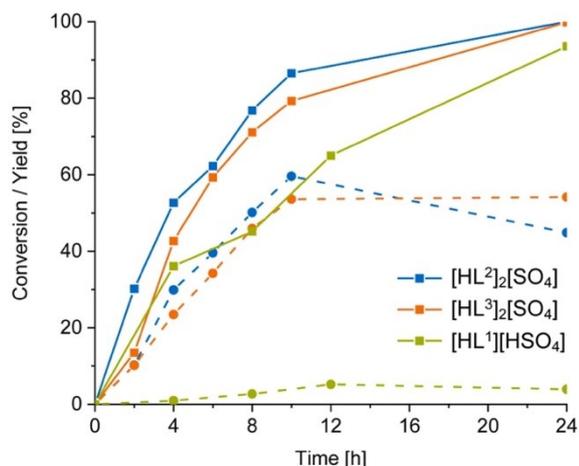
The supramolecular ion pairs  $[HL^1][HSO_4]$  and  $[HL^n]_2[SO_4]$  ( $n = 2, 3$ ), as well as the SIPs  $[M^n]_2[SO_4]$  obtained from amide and DHA, were tested as catalysts for the epoxidation of the model substrate cyclooctene (COE) at 80 °C with 5 mol% catalyst based on  $[HSO_4]^-$  or  $[SO_4]^{2-}$  using 2.5 equiv.  $H_2O_2$  (50 wt.% solution in water) as oxidant (Scheme 2). The SIPs were dissolved in the biphasic mixture aq.  $H_2O_2$ /COE at 80 °C upon stirring at 500 rpm. Aliquots were taken after certain time intervals and analyzed by GC-FID for quantification.



**Scheme 2.** Epoxidation of cyclooctene (COE) to cyclooctene oxide (COO) catalyzed by sulfate-SIPs using aq.  $H_2O_2$ . The molar ratio cat:COE:oxidant is 5:100:250.

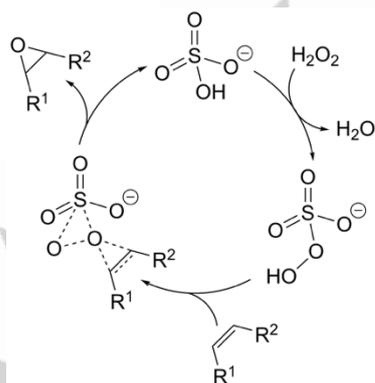
A comparison of the three SIPs prepared from the receptors and  $H_2SO_4$  shows that all SIPs are active catalysts for the epoxidation of COE to cyclooctene oxide (COO), with a quantitative conversion after 24 h observed for the benzamide derivative  $[HL^2][SO_4]$  (Figure 6). The SIP  $[HL^3][SO_4]$  exhibits a similar catalytic performance, albeit more slower, while the pyridinium-based SIP  $[HL^1][HSO_4]$  shows a decreased activity (93% conversion), most likely due to a lower concentration of the organic receptor anion  $[HL^1]^+$ , which is present in a 1:1 ratio to hydrogensulfate. The very low selectivity of  $[HL^1][HSO_4]$  towards COO (<5%) presumably originates from the acidic nature of the  $[HSO_4]^-$  anions, which are immediately hydrolyzing the epoxide to yield *trans*-1,2-cyclooctane diol, which was found to be the major byproduct. It should be noted here that in all experiments, no other products other than COE and COO were detected. For the catalysts  $[HL^2][SO_4]$  and  $[HL^3][SO_4]$ , the COO selectivities drop significantly over time owing to diol formation (55% and 45%,

respectively). The ring opening of the epoxide is expected to be catalyzed by the generally acidic nature of the ammonium functionalities of the SIPs. In contrast, this is not observed for the literature-reported perrhenate derivatives,<sup>[18]</sup> as their reactivity is at least three times higher at a lower reaction temperature.



**Figure 6.** Epoxidation of COE to COO by 5 mol% SIP (based on sulfate) at 80 °C using 2.5 equiv. 50 wt.%. H<sub>2</sub>O<sub>2</sub>. Bold lines: Conversion of COE, dashed lines: yield of COO.

Based on these results, and on the data obtained from the oxidation of sulfate to peroxymonosulfate (see the ESI-MS data in Figure 5), we propose the following mechanism for the epoxidation of olefins by sulfate SIPs (Scheme 3): the sulfate is first converted to hydrogensulfate, most likely owing to the acidity of hydrogen peroxide and, in the second step, the formation of peroxymonosulfate occurs. The active [HSO<sub>5</sub>]<sup>-</sup> species transfers an oxygen atom to the olefin substrate in a concerted manner, yielding the epoxide and the [HSO<sub>4</sub>]<sup>-</sup> anion.



**Scheme 3.** Proposed mechanism for the epoxidation of olefins by SIPs with sulfate as precatalyst. The SIP cations have been omitted for clarity.

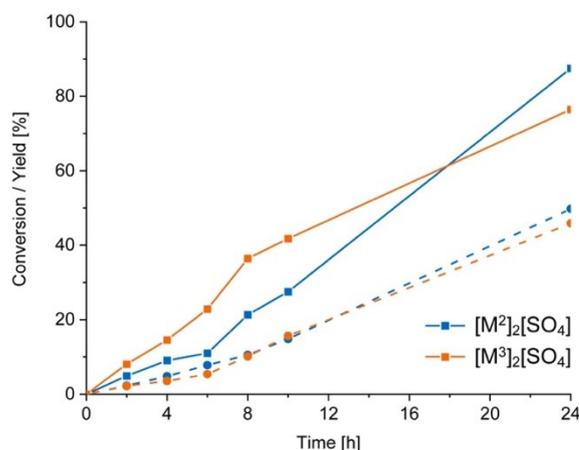
Much in contrast to the (hydrogen)sulfate SIPs, using simple salts such as sodium- or ammonium sulfate as catalysts and without any surfactants/phase transfer agents, only a marginal conversion of 7 % after 24 h in seen; this is the same as a blank experiment using pure solution of aq. H<sub>2</sub>O<sub>2</sub> and cyclooctene. These experiments clearly show that the epoxidation reaction does not take place in the aqueous phase due to the negligible

solubility of COE in hydrogen peroxide, and that a phase transfer agent, i.e., the cationic receptors HL<sup>n</sup>, and the supramolecular nature of the catalyst are required for the sulfate-catalyzed epoxidation in the organic phase.

Variations of the catalyst amount reveal the dependence of the selectivity with the acidity of the catalytic mixture, as the formation of the diol is further preferred by using catalyst concentrations higher than 5 mol% (SI, Table S1). A decrease of the SIP amount not only leads to a decreased activity but also affects the selectivity, as a longer reaction time and therefore a longer product stirring in the mixture negatively affects the selectivity towards cyclooctene oxide.

The stability of the catalytically applied SIPs was investigated by <sup>1</sup>H-NMR spectroscopy, revealing that the SIP [HL<sup>1</sup>][HSO<sub>4</sub>] remains intact after full conversion of the substrate, whereas the SIPs [HL<sup>n</sup>]<sub>2</sub>[SO<sub>4</sub>] (n = 2, 3) are fully transformed to a supramolecular network of the amide and dihexylammonium sulfate. Stability tests show that both receptors [HL<sup>2</sup>]<sup>+</sup> and [HL<sup>3</sup>]<sup>+</sup> are fully disassembled within 20 min under catalytic conditions (80 °C, 50 wt.% H<sub>2</sub>O<sub>2</sub>) to the respective amide and dihexylammonium sulfate (SI), while the byproduct, formaldehyde, could not be traced spectroscopically. Remarkably, the catalytic activities of both SIPs are retained over the full catalytic run and do not appear inactive.

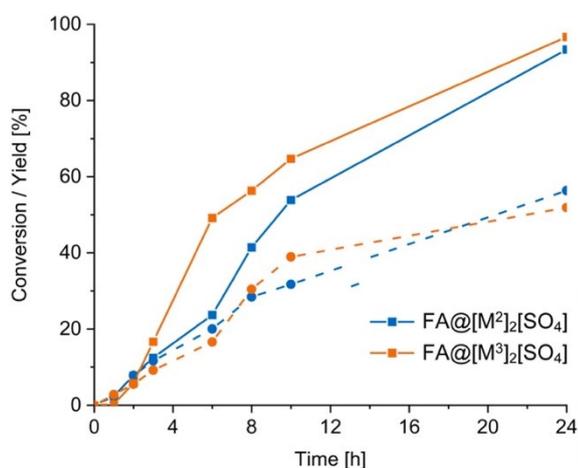
As such, the catalytic activity of the SIPs obtained from mixing an amide with dihexylammonium sulfate ([M<sup>n</sup>]<sub>2</sub>[SO<sub>4</sub>]) was examined in order to compare the performance with those of the SIPs obtained from the synthesized receptors ([HL<sup>n</sup>]<sub>2</sub>[SO<sub>4</sub>]). For this, the precursors benzamide or 3,3,5-trimethylhexanamide and dihexylammonium sulfate (mixtures [M<sup>2</sup>]<sub>2</sub>[SO<sub>4</sub>] and [M<sup>3</sup>]<sub>2</sub>[SO<sub>4</sub>], respectively, see Figure 7) were added to the biphasic mixture H<sub>2</sub>O<sub>2</sub>/COE and heated to 80 °C. Both catalyst systems exhibit a lower conversion after 24 h than in the case of the ([HL<sup>n</sup>]<sub>2</sub>[SO<sub>4</sub>]) SIPs (Figure 6), being 88% and 78%, respectively, with COO selectivities of 50% and 45%, respectively. Since our studies of the structure of the SIPs formed from the receptors L<sup>n</sup> (n = 2, 3) and H<sub>2</sub>O<sub>2</sub> have shown that the receptor structure is at least partially deconstructed and that formaldehyde must have formed, we investigated the possible influence of formaldehyde on the catalytic activity. Under oxidative conditions, reaction to performic acid and Prilezhaev-type epoxidations cannot be excluded a priori.



**Figure 7.** Epoxidation of COE to COO by 5 mol-% SIP [M<sup>n</sup>]<sub>2</sub>[SO<sub>4</sub>] (based on sulfate) at 80 °C using 2.5 equiv. 50 wt.%. H<sub>2</sub>O<sub>2</sub>. Bold lines: Conversion of COE, dashed lines: yield of COO.

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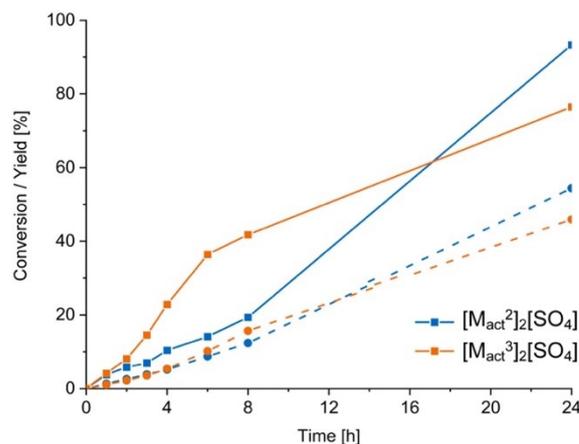
To examine the contribution of formaldehyde (FA) to the epoxidation of COE, 5 mol% of FA was added to a pure biphasic COE/H<sub>2</sub>O<sub>2</sub> mixture, showing a COE conversion of 23%. In the next step, we studied the activity of a mixture of formaldehyde and the SIPs [M<sup>2</sup>]<sub>2</sub>[SO<sub>4</sub>] and [M<sup>3</sup>]<sub>2</sub>[SO<sub>4</sub>], respectively. The catalytic performances of these mixtures FA@[M<sup>n</sup>]<sub>2</sub>[SO<sub>4</sub>], shown in Figure 8, are similar compared with those of the SIPs [HL<sup>n</sup>]<sub>2</sub>[SO<sub>4</sub>] (n = 2, 3) shown in Figure 6; however, an initiation period of about 1-2 h is evident. This finding shows that the presence of FA is the reason for the difference in catalytic COE conversions between the SIPs [HL<sup>n</sup>]<sub>2</sub>[SO<sub>4</sub>] obtained from the receptors (Figure 6) and those obtained from the amide/DHA mixture SIPs [M<sup>n</sup>]<sub>2</sub>[SO<sub>4</sub>] (Figure 7). These experiments underline that simple chemical precursors are able to form a highly sophisticated metal-free catalyst for olefin epoxidation in a biphasic reaction mixture, synergizing the effects of anion phase-transfer and H<sub>2</sub>O<sub>2</sub> activation. Similarly to the SIPs originating from the synthesized receptors L<sup>n</sup> (n = 1, 2, 3), an application of 5 mol% [M<sup>n</sup>]<sub>2</sub>SO<sub>4</sub> (n = 2, 3) is a good compromise of activity and selectivity (SI; Table S2).



**Figure 8.** Epoxidation of COE to COO by 5 mol-% SIP (based on sulfate) and 10 mol% formaldehyde (FA) at 80 °C using 2.5 equiv. 50 wt.% H<sub>2</sub>O<sub>2</sub>. Bold lines: Conversion of COE, dashed lines: yield of COO.

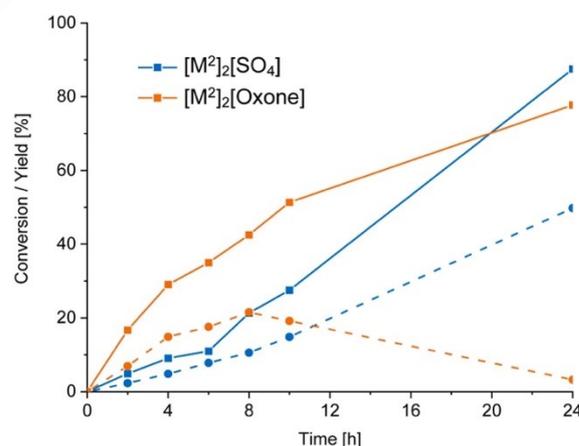
The DLS results reveal that the formation of the crystallographically determined supramolecular structure of [M<sup>2</sup>]<sub>2</sub>[SO<sub>4</sub>] may require heating at elevated temperatures. To investigate a possible catalytic initiation period, we stirred the reaction mixture overnight at 80 °C prior to addition of H<sub>2</sub>O<sub>2</sub>, eventually starting the reaction. Comparison of the catalytic activity with and without this pre-activation yields similar performances, suggesting that the respective SIP is formed immediately or other feasible aggregates are similar in activity and selectivity (Figures 7 and 8).

To demonstrate the catalytic activity of peroxymonosulfate as part of the SIP in the organic phase without any other peroxy intermediates (such as dioxiranes from ketones), we used commercially available Oxone® as oxidant under anhydrous conditions to avoid H<sub>2</sub>O<sub>2</sub> evolution. The high acidity of the triple-salt KHSO<sub>5</sub> · 0.5 KHSO<sub>4</sub> · 0.5 K<sub>2</sub>SO<sub>4</sub> was buffered with stoichiometric amounts dihexylamine in presence of benzamide, leading to formation of the persulfate-SIP. Due to the required application of the SIP as stoichiometric oxidant, cyclooctene,



**Figure 9.** SIP- activation in COE for 18 h at 80 °C; Epoxidation of COE to COO by 5 mol% SIP (based on sulfate) at 80 °C using 2.5 equiv. 50 wt.% H<sub>2</sub>O<sub>2</sub>. Bold lines: Conversion of COE, dashed lines: yield of COO.

which is expected to have no different influence on the SIP formation, is used to dilute cyclooctene to achieve SIP-concentrations in the organic phase as investigated above. The slurry was stirred at 80 °C and the activity was shown to be similar to that of the sulfate-catalyzed epoxidation using H<sub>2</sub>O<sub>2</sub> as oxidant (Figure 9), yet with a significantly lower selectivity. This result shows that (i) peroxymonosulfate is the active species of the epoxidation and (ii) Oxone® has no advantage as oxidant since H<sub>2</sub>O<sub>2</sub> is more convenient, as effective and much 'greener' due to the lack of waste salts. It needs to be noted here that per gram of COE, three grams of Oxone® are required for epoxidation, compared with <0.5 mL H<sub>2</sub>O<sub>2</sub> (50 wt.%), which releases water and can easily be removed afterwards due to the biphasic nature of the reaction.



**Figure 9.** Comparison of the reactivities of Oxone and hydrogen peroxide as oxidants in the epoxidation of cyclooctene at 80 °C. Bold lines: conversion; dashed lines: yield.

We further investigated a scope of substrates exhibiting different C=C double bond substitution- and configuration patterns using the [M<sup>2</sup>]<sub>2</sub>SO<sub>4</sub> SIP as catalysts (Table 2). The highest reactivity and selectivity towards olefins with a *cis* substituent configuration are

seen, especially for the ring-strained cyclic six-membered olefins cyclohexene and 1-methylcyclohexene. *Cis*-2-octene has a higher reactivity than the *trans* derivative, which is owed to the easier approach of the persulfate oxidant to the double bond. The terminal olefin 1-octene shows moderate conversion, but low epoxide selectivity due to facile epoxide ring opening. The conversion of styrene is similar, but shows no traces of the epoxide due to the electron-withdrawing phenyl substituent and hence to a facile ring opening. Here, traces of the side-products benzaldehyde and benzoic acid were detected, which arise from oxidative diol cleavage of the hydrolyzed follow-up product phenylethanediol.

**Table 2.** Substrate variation with 5 mol%  $[M^2]_2[SO_4]$  and 2.5 equiv.  $H_2O_2$ .

Substrate	Time [h]	Conv. [%]	Sel. [%] <sup>[a]</sup>
Cyclohexene	4	91	84
1-Methylcyclohexene	4	93	77
1-Octene	24	79	4
<i>cis</i> -2-Octene	24	91	18
<i>trans</i> -2-octene	24	57	18
Styrene	12	73	0
Cyclooctene	24	88	57

[a] GC-MS reveals that diols are the only side-product except for styrene, which forms traces of benzaldehyde and benzoic acid.

## Conclusion

In this study, we have presented the assembly of sulfate-based supramolecular ion pairs (SIPs) for the epoxidation of non-polar olefins using aqueous hydrogen peroxide under biphasic conditions. This is achieved by the transfer of the highly polar sulfate species into the organic phase by sophisticated organic receptors that form SIPs. Remarkably, these elaborate receptors do not necessarily need to be synthesized prior to use, as the single components are shown to spontaneously assemble to provide catalysts with the same intrinsic reactivity.

While these SIPs cannot compete with sophisticated and expensive metal complexes in terms of activity, the abundance of sulfuric acid as well as the simplicity of the organic SIP precursors (e.g., benzamide and dihexylamine) render this system highly competitive. The major advantage of using hydrogen peroxide is its 'green' character, releasing water as only byproduct, in contrast to huge quantities of chemical waste from more traditional and stoichiometric persulfate salts. This biphasic catalyst approach with sulfate SIPs allows for the use of environmentally benign hydrogen peroxide, forming and transferring peroxymonosulfate to the organic substrate phase without the need of solvents besides water, which can be removed after the reaction by decantation.

Ongoing investigations address the structural SIP optimization to enhance the catalytic activity and selectivity as well as to trigger the phase behavior by external stimuli such as temperature and

the concentration of  $H_2O_2$  for an efficient recycling procedure for the catalyst. Nevertheless, the findings in this study indicate the right way forward for sustainable oxidation reactions exploiting supramolecular catalyst approaches.

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[17a,17b,20–26]</sup>

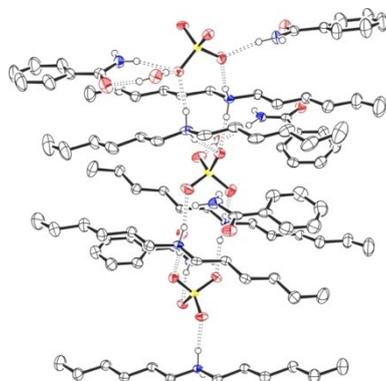
## Acknowledgements

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**Keywords:** Sulfate • Molecular Catalysis • Supramolecular Chemistry • Epoxidations • H-Bonding

- [1] a) A. K. Yudin, *Aziridines and Epoxides in Organic Synthesis*, Wiley, Weinheim, **2006**; b) K. Bryliakov, *Environmentally Sustainable Catalytic Asymmetric Oxidations*, CRC Press, Boca Raton, **2014**; c) S. A. Hauser, M. Cokoja, F. E. Kühn, *Catal. Sci. Technol.* **2013**, *3*, 552–561.
- [2] a) B. S. Lane, K. Burgess, *Chem. Rev.* **2003**, *103*, 2457–2473; b) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329–2363; c) Q.-H. Xia, H.-Q. Ge, C.-P. Ye, Z.-M. Liu, K.-X. Su, *Chem. Rev.* **2005**, *105*, 1603–1662.
- [3] T. Hashimoto, K. Maruoka, *Chem. Rev.* **2007**, *107*, 5656–5682; b) T. Ooi, K. Maruoka, *Angew. Chem. Int. Ed.* **2007**, *46*, 4222–4266; c) Y. Zhu, Q. Wang, R. G. Cornwall, Y. Shi, *Chem. Rev.* **2014**, *114*, 8199–8256.
- [4] a) P. T. Anastas, M. M. Kirchhoff, *Acc. Chem. Res.* **2002**, *35*, 686–694; b) P. Anastas, N. Eghbali, *Chem. Soc. Rev.* **2010**, *39*, 301–312; c) P. G. Jessop, *Green Chem.* **2011**, *13*, 1391; d) R. A. Sheldon, *Green Chem.* **2017**, *19*, 18–43; e) J. B. Zimmerman, P. T. Anastas, H. C. Erythropel, W. Leitner, *Science* **2020**, *367*, 397–400.
- [5] F. Schmidt, M. Cokoja, *Green Chem.* **2021**, *23*, 708–722; b) M. Hegelmann, F. Schmidt, M. Cokoja, *Encyclopedia of Inorganic and Bioinorganic Chemistry*, Wiley, accepted.
- [6] a) M. Cokoja, R. M. Reich, M. E. Wilhelm, M. Kaposi, J. Schäffer, D. S. Morris, C. J. Münchmeyer, M. H. Anthofer, I. I. E. Markovits, F. E. Kühn, W. A. Herrmann, A. Jess, J. B. Love, *ChemSusChem* **2016**, *9*, 1773–1776; b) J. Schäffer, M. Alber, W. Korth, M. Cokoja, A. Jess, *ChemistrySelect* **2017**, *2*, 11891–11898.
- [7] F. Schmidt, B. Zehner, W. Korth, A. Jess, M. Cokoja, *Catal. Sci. Technol.* **2020**, *10*, 4448–4457.
- [8] I. I. E. Markovits, W. A. Eger, S. Yue, M. Cokoja, C. J. Münchmeyer, B. Zhang, M.-D. Zhou, A. Genest, J. Mink, S.-L. Zang, N. Rösch, F. E. Kühn, *Chem. Eur. J.* **2013**, *19*, 5972–5979.
- [9] F. Schmidt, B. Zehner, M. Kaposi, M. Drees, J. Mink, W. Korth, A. Jess, M. Cokoja, *Green Chem.* **2021**, *23*, 1965–1971.
- [10] Studies with surface-active imidazolium sulfates, -hydrogensulfates and -alkylsulfates as catalysts for the epoxidation of cyclooctene in water using hydrogen peroxide as oxidant have shown that in water after a short period of time numerous C–H and C–C bond activation products are formed. See: J. Berger, Master's Thesis, Technical University of Munich, **2018**.
- [11] R. Bloch, J. Abecassis, D. Hassan, *J. Org. Chem.* **1985**, *50*, 1544–1545.
- [12] W. Zhu, W. T. Ford, *J. Org. Chem.* **1991**, *56*, 7022–7026.
- [13] H.-Y. Shu, *J. Chem. Technol. Biotechnol.* **2005**, *80*, 273–280.

- [14] P. Zawadski, K. Matuszek, W. Czardybon, A. Chrobok, *New J. Chem.* **2015**, *39*, 5282–5286.
- [15] D. Jaglencic, Ł. Dobrzycki, M. Karbarz, J. Romański, *Chem. Sci.* **2019**, *10*, 9542–9547.
- [16] M. Wilson, P. J. Bailey, P. A. Tasker, J. R. Turkington, R. A. Grant, J. B. Love, *Chem. Soc. Rev.* **2014**, *43*, 123–134.
- [17] a) J. R. Turkington, V. Cocalia, K. Kendall, C. A. Morrison, P. Richardson, T. Sassi, P. A. Tasker, P. J. Bailey, K. C. Sole, *Inorg. Chem.* **2012**, *51*, 12805–12819; b) R. J. Ellis, J. Chartres, D. K. Henderson, R. Cabot, P. R. Richardson, F. J. White, M. Schröder, J. R. Turkington, P. A. Tasker, K. C. Sole, *Chem. Eur. J.* **2012**, *18*, 7715–7728.
- [18] M. Cokoja, I. I. E. Markovits, M. H. Anthofer, S. Poplata, A. Pöthig, D. S. Morris, P. A. Tasker, W. A. Herrmann, F. E. Kühn, J. B. Love, *Chem. Commun.* **2015**, *51*, 3399–3402.
- [19] R. A. Aitken, S. Arumugam, S. T. E. Mesher, F. G. Riddell, *J. Chem. Soc., Perkin Trans. 2* **2002**, 225–226.
- [20] APEX suite of crystallographic software. APEX 3. Version 2015-5.2. Bruker AXS Inc., Madison, Wisconsin, USA, **2015**.
- [21] SAINT. Version 8.34A. Bruker AXS Inc., Madison, Wisconsin, USA, **2014**.
- [22] SADABS. Version 2014/5., Bruker AXS Inc., Madison, Wisconsin, USA, **2014**.
- [23] G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
- [24] G. M. Sheldrick, SHELXT - integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.
- [25] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [26] Momma, K. & Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Cryst.* **2011**, *44*, 1272–1276.

**Entry for the Table of Contents**

Supramolecular host-guest assemblies of sulfate ions and amidammonium receptor cations are shown to act as catalysts for olefin epoxidation by hydrogen peroxide under biphasic conditions, showing the first case of sulfate ions being used as catalyst by conversion to peroxymonosulfate.