



Thioanisole oxidation with hydrogen peroxide catalyzed by hexadentate 8-quinolinolato manganese(III) complexes

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ABSTRACT

Hexadentate 8-quinolinolato manganese(III) complexes (Q_3Mn^{III}) developed by us, with the help of NH_4OAc and $HOAc$, were found to efficiently catalyze the mild oxidation of thioanisole with aqueous hydrogen peroxide in environmentally benign acetone–water media. The ligand's halogen substituents could improve the catalytic efficiency of Q_3Mn^{III} complexes, and this is likely that they can strengthen the distorted effect of Q_3Mn^{III} , as supported by B3LYP/6-311G (d) calculation. The adjusting effect of additives on this sulfoxidation was also investigated and their mediation mechanisms were proposed.

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Oxidation of thioethers is an important reaction in organic synthesis [1,2], being due to the reaction products—sulfoxides and sulfones, which are increasingly used as agrochemicals, drug, and synthetic intermediates [3–5]. Therefore, there has been considerable interest in the development of highly efficient sulfoxidation catalysts [6–20]. In particular, the non-toxic transition metals such as Mn-mediated sulfoxidation with aqueous hydrogen peroxide (H_2O_2) have been appreciated as a green process [21]. However, the efficient Mn-mediated sulfoxidation systems reported to date have mainly used tetradentate binding manganese complexes as catalysts [21–24] and have one or more disadvantages, such as the use of expensive $PhIO$ or anhydrous H_2O_2 as oxidant and the toxic chlorohydrocarbon solvents.

Recently, we became interested in the use of hexadentate binding 8-quinolinolato manganese (III) complexes (Q_3Mn^{III}) presented in Scheme 1) as oxidation catalysts and have found the Q_3Mn^{III} could efficiently catalyze olefin epoxidations [25,26], and alcohol oxidations [27] with H_2O_2 in green acetone–water or pure acetone medium. Based on the recent successful applications of Q_3Mn^{III} catalysts in both the oxidation reactions mentioned above, we became interested in the potential of the Q_3Mn^{III} catalysts for sulfide oxidation. Herein, for the first time we report the initial results obtained from employing the Q_3Mn^{III} complexes to catalyze thioanisole sul-

foxidation with aqueous H_2O_2 in water–acetone media containing ammonium acetate (NH_4OAc) and acetic acid ($HOAc$).

1. Experimental

1.1. Preparation and characterization of Q_3Mn^{III} complexes

Q_3Mn complexes are prepared and characterized following the reported procedure [26]. The preparation of a tetradentate binding 5,7-dibromo-8-quinolinolato Mn^{II} (Q_2Mn^{II}) is described as follows, 5 ml of $Mn(OAc)_2$ aqueous solution (1 mol L^{-1}) was added dropwise to 50 ml of stirred THF containing 10 mmol of 5,7-dibromo-8-hydroxyquinoline. Then, the reaction mixture was refluxed for 2 h, and the resulting precipitate was filtrated and washed with ethanol for at least three times. After air-drying, a slight-yellow solid (90% yield) was obtained and denoted as Q_2Mn^{II} . And a traditional salen- $Mn^{III}Cl$ was also synthesized from N,N -bis(salicylidene)ethylethylenediamine and $MnCl_2$ following reported procedures [21].

1.2. Oxidation procedure

The general procedure for sulfoxidations is described as follows. To a cooled (10°C) and stirred water–acetone (v/v, 1:3, 3 ml) mixture of thioether (1 mmol), catalyst Q_3Mn^{III} (0.002 mmol), NH_4OAc (0.2 mmol), and $HOAc$ (0.1 mmol), 30% H_2O_2 (1.3 mmol) was added dropwise during an appointed period (generally within half an

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hour) in order to improve the utilization efficiency of H_2O_2 . After H_2O_2 was consumed completely *via* an inspection with potassium iodide–starch test paper, the catalyst was separated from the reaction mixture by filtration, and the filtrate was analyzed on an Agilent 6890N gas chromatography (GC) with a HP-5 quartz capillary column ($30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$) and flame ionization detector (FID) using ultrapure nitrogen as carrier gas (rate 1.0 mL/min). Both the injector and detector temperature were $250\text{ }^\circ\text{C}$, and the column temperature was between 160 and $200\text{ }^\circ\text{C}$. The isolated sulfoxide and sulfone were satisfactorily identified by comparing their MS spectra with those of the authentic samples.

2. Results and discussion

2.1. Characterization of $\text{Q}_3\text{Mn}^{\text{III}}$ complexes

In our previous works, we have proven that the $\text{Q}_3\text{Mn}^{\text{III}}$ complexes (**1a–1e**) own a hexadentate structure with the distorted octahedral geometry *via* CHN and Mn elemental analyses, as well as a diffuse reflectance UV–vis spectroscopy technique [25,26]. Here, the distortion effect of the $\text{Q}_3\text{Mn}^{\text{III}}$ complexes are further investigated by means of the density functional theory method (B3LYP) with 6-311G(d) basis set, where all the calculations were conducted on the Ganssian-03 version C02 package with tight self-consistent field (SCF) convergence and ultrafine integration grids. Fig. 1 gives the optimized three-dimensional structures and the calculated Mn–O bond distances for **1a** and **1d**, wherein three Mn–O bonds of each complex are not equal to each other, and the Mn1–O2 bond is the longest among the Mn–O bonds. Moreover, the difference among the Mn–O bonds appears more obvious upon **1d** compared to **1a** (see Δ value listed in Fig. 1), which should be due to a stronger distortion effect of 5,7-dibrominated $\text{Q}_3\text{Mn}^{\text{III}}$.

2.2. Catalytic sulfoxidation

The catalytic performances of $\text{Q}_3\text{Mn}^{\text{III}}$ complexes were checked *via* thioanisole oxidation with 30% aqueous H_2O_2 and the results are listed in Table 1. All the $\text{Q}_3\text{Mn}^{\text{III}}$ complexes (**1a–1e**) as shown in entries 1–5, were active to this reaction and could show modest to high activity and good selectivity for the sulfoxide in water–acetone media containing NH_4OAc – HOAc . Notably, a favorable effect of the

halogen substituents of ligand's aryl ring on catalytic activity could be noticed upon **1b–1e** (see entries 2–5), and 5,7-dibrominated $\text{Q}_3\text{Mn}^{\text{III}}$ (**1d**) achieved the best catalytic efficiency (TON=466), which is likely due to an enhancing distortion effect of the halogenated $\text{Q}_3\text{Mn}^{\text{III}}$, as supported by the above theoretical calculation. The reuse of representative catalyst **1d** was checked *via* thioanisole oxidation, wherein **1d** could be conveniently filtered from the reaction media and reused twice without loss of activity (entry 6), indicating that **1d** catalyst owns a good stability. Entry 7 illustrates that a fivefold scale-up reaction for thioanisole showed approximate results as the small-scale one, and could achieve 56% of isolated yield for sulfoxide by column chromatography. It is noteworthy that using a tetradentate $\text{Q}_2\text{Mn}^{\text{II}}$ gave a relatively low conversion compared to the corresponding hexadentate $\text{Q}_3\text{Mn}^{\text{III}}$ **1d** (entry 8), and a much lower conversion was noticed using a traditional salen– $\text{Mn}^{\text{III}}\text{Cl}$ catalyst (entry 9). Entries 10 and 11 further illustrate that **1d** was very effective for the oxidation of 4-chlorothioanisole and 4-bromothioanisole although such halogen substituents could lead to a slight decrease in sulfoxide yield. By the way, thioanisole could be directly and completely oxidized to its sulfoxide (74%) and sulfone (26%) by 1.3 equivalence of peracetic acid (entry 12).

The effects of additives were further investigated by using the most efficient **1d** as a catalyst (entries 13–16). It is evident that **1d** showed relatively low catalytic efficiency in the absence of additives (entry 13). Among the additives examined, HOAc was effective to improve sulfoxide yield, provided that reaction time was prolonged (entry 14 vs. entry 13). NH_4OAc could obviously accelerate the reaction, but slightly lower sulfoxide selectivity (entry 15). And the best result could be obtained on the coexistence of NH_4OAc and HOAc (entry 4). It is noteworthy that Na_2HPO_4 could also promote the reaction, but significantly lowers the selectivity (entry 16). These findings indicate that the mediated effect of the additives on the $\text{Q}_3\text{Mn}^{\text{III}}$ catalytic system is different to each other.

In the following experiment, the effect of H_2O_2 amount on conversion and sulfoxide selectivity was investigated using **1d**-catalyzed thioanisole oxidation. As shown in Fig. 2, the conversion drastically increases and sulfoxide selectivity smoothly decreases with the molecular ratio of H_2O_2 to thioanisole until such ratio being 1.3. Any attempt to increase the ratio of H_2O_2 actually resulted in decreased yield, in consequence of sulfoxide to be further oxidized to the corresponding sulfone.

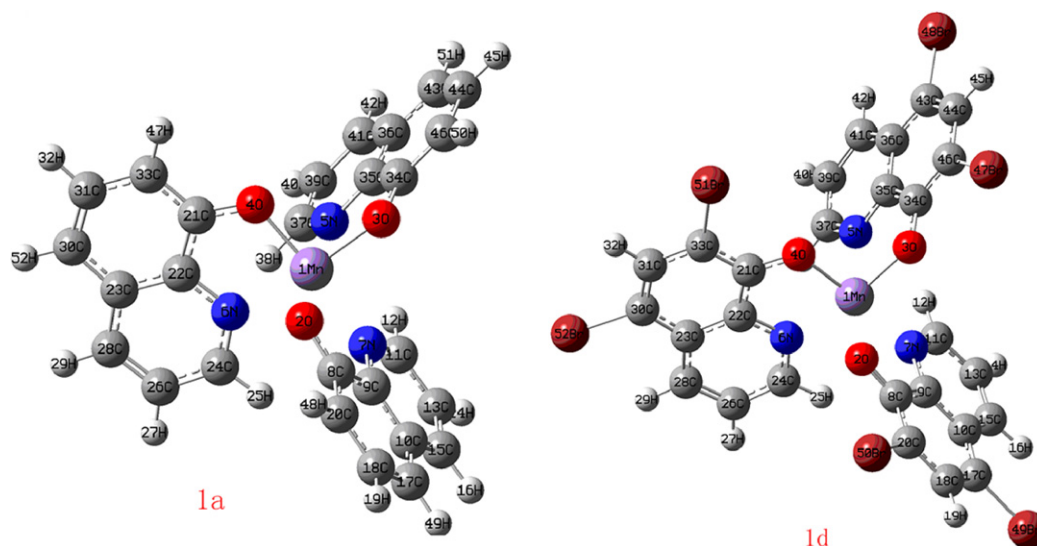
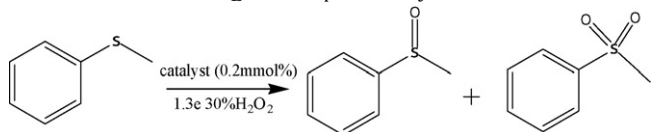


Fig. 1. The optimum three dimensional structures of $\text{Q}_3\text{Mn}^{\text{III}}$ complex **1a** and **1d**. Here, the Mn–O bond distances (Å) of **1d** are listed as follows (the data listed in the bracket are the corresponding Mn–O bond distances of **1a**): Mn1–O2, 2.0664 (2.0655); Mn1–O3, 1.8889 (1.8882); Mn1–O4, 1.8943 (1.8956); Δ value = Mn1–O2 – (Mn1–O3 + Mn1–O4)/2 = 0.1748 (0.1736).

Table 1
The results obtained from Q_3Mn^{III} complexes catalyzed thioanisole oxidation^a.



Entry	Catalyst	Additives (mmol)	Time (h)	Conv. (%)	Sel. ^b (%)	TON
1	1a		2	76	82	380
2	1b		3	87	74	290
3	1c		2	87	73	436
4	1d		2	93	71	466
5	1e	NH ₄ OAc	2	84	76	420
6 ^c	1d	(0.2)+HOAc	2	92 (93)	67 (60)	460 (466)
7 ^d	1d	(0.1)	2	88	72 (56)	440
8	Q_2Mn^{II}		1	86	69	430
9	Salen-Mn ^{III}		2	41	85	205
10 ^e	1d		2	92	63	460
11 ^f	1d		5	89	70	445
12 ^g	No catalyst	No additive	1	99	74	
13	1d	No additive	18	21	80	108
14	1d	HOAc (0.1)	24	45	86	216
15	1d	NH ₄ OAc (0.2)	2	93	62	466
16	1d	Na ₂ HPO ₄ (0.2)	12	60	34	300

^a Reaction conditions: thioanisole (1 mmol), catalyst (0.2 mol%), 30% H₂O₂ (1.3 mmol) and water/acetone (1/3, 3 ml) at 10 °C. Conversion and selectivity were determined by GC. TON = (mol of thioanisole oxidized)/(mol of catalyst).

^b Selectivity for sulfoxide.

^c Data comes from using the **1d** recovered once and twice, in which the data in parentheses present the results of the second cycle.

^d Fivefold scale-up, and data in parentheses are the isolated yield for sulfoxide by column chromatography.

^e 4-Chlorothioanisole as a substrate.

^f 4-Bromothioanisole as a substrate.

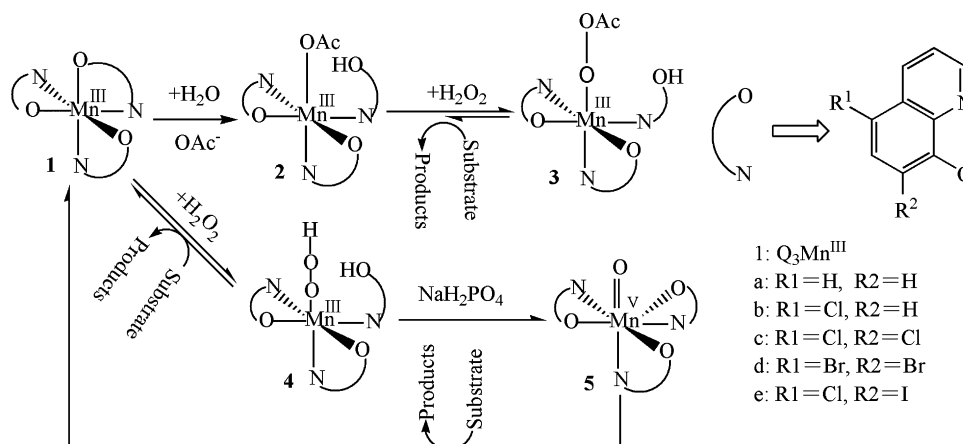
^g Reaction conditions: thioanisole (1 mmol), 15% HOAc (1.3 mmol) and water/acetone (1/3, 3 ml) at 10 °C.

2.3. Mechanism

In order to investigate the catalytic mechanism for the Q_3Mn^{III} -catalyzed thioanisole oxidation, a stepwise overlay of UV-vis spectra for **1d** complex in acetone medium at room temperature is illustrated in Fig. 3. Wherein A is the spectrum of **1d** in acetone where an absorption band with $\lambda_{max} \sim 412$ nm is assigned to the metal to ligand charge transfer (MLCT) [28]. When NH₄OAc-HOAc aqueous solution was added to the A solution, such MLCT band decreased a little (see B). Followed by adding H₂O₂ to the B solution, the MLCT band immediately shifted to $\lambda_{max} \sim 424$ nm, its intensity decreased a lot (see C), being likely due to the rapid formation of some Mn^{III} peroxy species X, as proposed by Yamada et al. for the reaction with molecular oxygen with (salen)Mn(III) in the presence of an aldehyde [29] and by Pietikäinen for (Salen)Mn(III)-catalyzed epoxidation of alkenes with hydrogen peroxide in the presence of

carboxylate salt cocatalyst [30]. By the way, we also found such X species in the presence of only NH₄OAc additive (see an inset in Fig. 3). Adding thioanisole to the C further, such band at $\lambda_{max} \sim 424$ nm ascended in 1 h (see D) and then slowly descended in the following 1 h (see E), finally, it rebounded toward the trace B and a very strong absorbance at $\lambda_{max} \sim 330$ nm, attributed to the oxidation products (sulfoxide and sulfone), could simultaneously appear at 8 h (see F), implying that the X species could eventually return to the original Q_3Mn^{III} status through transferring its O atom to thioanisole. It is noteworthy that the trace in 500–600 nm, being assigned to the ligand to metal charge transfer of the $Q_3Mn^{V=O}$, did not ascend in the whole process, indicating that the $Q_3Mn^{V=O}$ should not be mainly responsible for the present oxidation process.

Fig. 4 illustrates the UV-vis spectral change of **1d**-catalyzed thioanisole oxidation system in the absence of additive, wherein G is the spectrum of **1d** in acetone-water solution containing 0.2 mmol



Scheme 1. Possible catalytic pathways for Q_3Mn^{III} -catalyzed sulfoxidation.

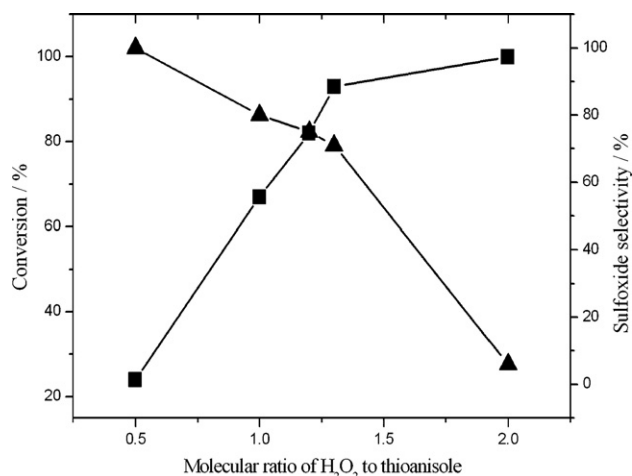


Fig. 2. The H₂O₂/thioanisole molecular ratio-dependent conversion and sulfoxide selectivity for **1d**-catalyzed the oxidation of thioanisole with hydrogen peroxide.

thioanisole. When adding H₂O₂ to the G solution, the MLCT band decreased a lot and simultaneously brought a slight blue shift (see H). This spectral change may be due to the formation of another Mn^{III} peroxy species Y, which is different from the X species mentioned above. Successively, such band continuously descended with time (see I and J) and finally became an obscure broad peak after 8 h (see K), perhaps indicating that catalyst degradation easily occurred in the absence of additive. Notably, using HOAc as an additive could also give the Y species rather than the expected X one, and this is likely due the weak ionization degree of HOAc in the reaction media; But HOAc could obviously alleviate the Y species decay (see inset in Fig. 4), illustrating that it is favorable of stabilizing the Y species.

Interestingly, in the presence of Na₂HPO₄ additive, its spectral change has an outstanding feature different from those mentioned above, wherein the formation and then disappearance of the Q₃Mn^V=O species could be clearly observed (see N and O in Fig. 5), supporting that the Q₃Mn^V=O should be responsible for the transfer of its O atom to thioanisole.

Based on the above findings, we propose that the reaction pathway of Q₃Mn^{III}-catalyzed thioanisole oxidation is dependent on the

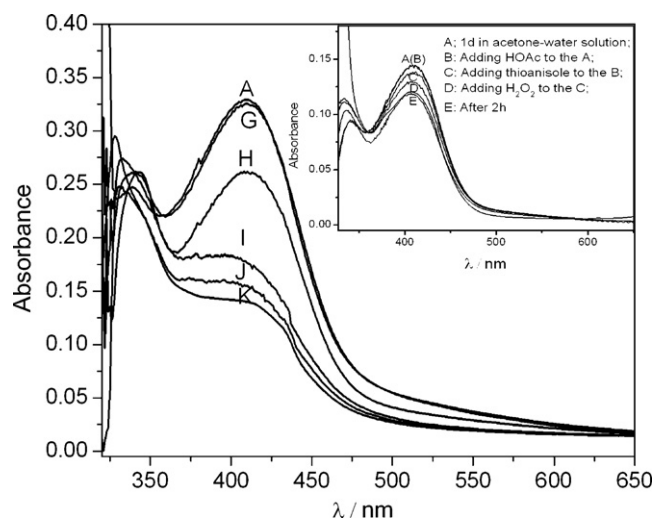


Fig. 4. UV-vis spectra of (A) a solution of **1d** in acetone (1.0×10^{-6} M, 4 ml); (G) adding 0.02 mmol thioanisole to the solution A; (H) adding 30% H₂O₂ (8 equiv. relative to **1d**) to the solution G; (I) 0.5 h later; (J) 1 h later; (K) 8 h later. Inset illustrates a spectral change of **1d**-catalyzed thioanisole oxidation with H₂O₂ in the presence of HOAc.

additives used. Specifically, in the presence of NH₄OAc–HOAc or NH₄OAc, the Q₃Mn^{III} (**1** in Scheme 1) easily cleaves the longest Mn–O bond to form a pentadentate Q₃Mn^{III}–OAc with a pendant hydroxyl group (**2**) [26]. Then, **2** rapidly interacts with H₂O₂ to form the corresponding Q₃Mn^{III}–OOAc (the above X species, see **3** in Scheme 1). The **3** may eventually return to the **2** through directly transferring its O atom to thioanisole due to its good oxidation capacity [29,31], as supported by the above experiment of using peracetic acid as an oxidant in the absence of catalyst (entry 12 in Table 1). On the other hand, the **1** may directly react with H₂O₂ to form a pentadentate Q₃Mn^{III}–OOH species in the absence of additives (the above Y species, see **4**) [27]. Then, the **4** may transfer its O atom to thioanisole through a homolytic cleavage of its O–OH bond to radicals in solution, which leads to spurious reactions that can degrade the catalyst, as observed by the above catalytic experiment and spectral change. However, the **4**, with the help of NaH₂PO₄, is easily converted to a Q₃Mn^V=O species (**5**) through a heterolytic cleavage of its O–OH bond, and then, the **5** as a strong oxidant [32],

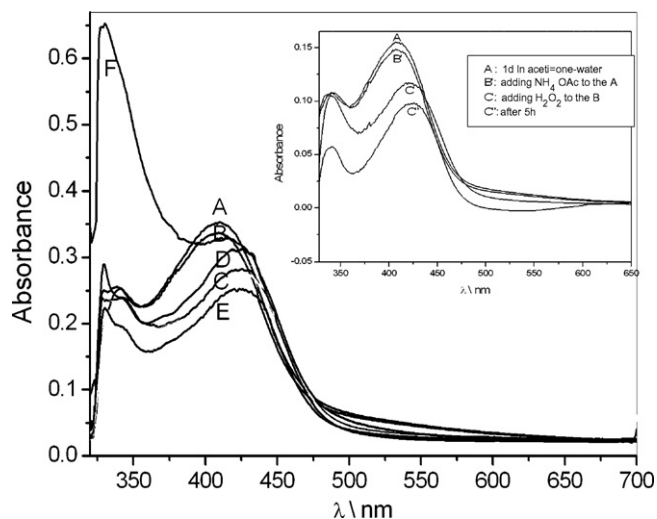


Fig. 3. UV-vis spectra of (A) a solution of **1d** in acetone (1.0×10^{-6} M, 4 ml); (B) adding 0.04 mmol NH₄OAc and 0.02 mmol HOAc aqueous solution; (C) adding 30% H₂O₂ (8 equiv. relative to **1d**) to the solution B; (D) 1 h later of adding 0.02 mmol thioanisole to the solution C; (E) 2 h later; (F) 8 h later. Inset illustrates a spectral change of H₂O₂-treated **1d** in the presence of NH₄OAc.

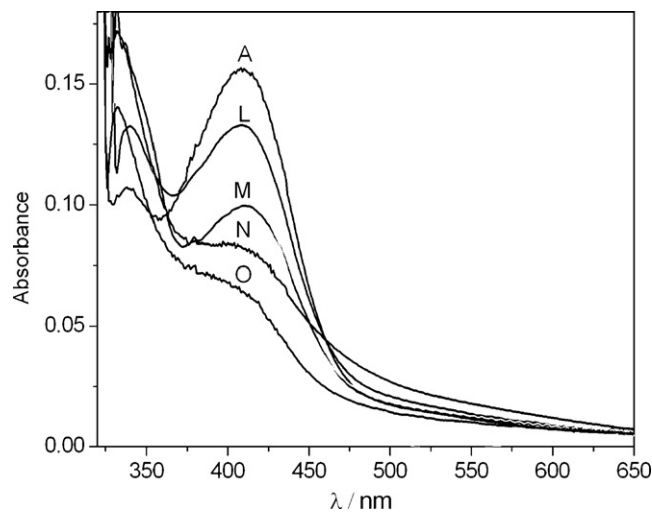


Fig. 5. UV-vis spectra of (A) a solution of **1d** in acetone (1.0×10^{-6} M, 4 ml); (L) adding 0.02 mmol of Na₂HPO₄ aqueous solution to the solution A; (M) adding 0.02 mmol thioanisole to the solution L; (N) 10 min later of adding 30% H₂O₂ (8 equiv. relative to **1d**) to the solution M; (O) 2 h later.

may directly oxidize thioanisole to the oxidation products containing more sulfone (ca. 66%), and simultaneously give the regenerated catalyst.

In conclusion, for the first time we have developed an efficient and environmentally friendly method for thioanisole oxidation with H₂O₂ catalyzed by hexadentate Q₃Mn^{III} complexes in acetone–water media, and proposed different reaction pathways for the various additives-mediated Q₃Mn^{III} catalytic oxidation system. Having found this kind of Q₃Mn^{III} complexes, we are interested in exploiting the preparations of other 8-quinolinolato metal complexes and their potential applications in organic synthesis.

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