Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Preparation, Characterization and Reactivity of a Bis-hypochlorite Adduct of a Chiral Manganese(IV) Salen Complex

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S Supporting Information

ABSTRACT: A bis-hypochlorite adduct of a manganese-(IV) salen complex having a chiral (R,R)-cyclohexane-1,2diamine linkage $(2^{-t}Bu)$ is successfully prepared and characterized by various spectroscopic methods. The reactions of $2^{-t}Bu$ with various organic substrates show that $2^{-t}Bu$ is capable of sulfoxidation, epoxidation, chlorination, and hydrogen abstraction reactions. However, the enantioselectivity of the epoxidation reactions by $2^{-t}Bu$ is much lower than that reported for the catalytic reactions by Jacobsen's catalyst. The low enantioselectivity is consistent with a planar conformation of the salen ligand, which is suggested by circular dichroism spectroscopy. This study suggests that $2^{-t}Bu$ is not a reactive intermediate of Jacobsen's enantioselective epoxidation catalysis.

ransition-metal-catalyzed oxygenation reactions have received much attention because of their demand in organic synthetic strategies and their biological relevance with respect to metalloenzymes.¹⁻⁷ These catalytic oxygenation reactions are initiated by the reactions of transition-metal catalysts with terminal oxidants such as hydrogen peroxide, iodosylarene, sodium hypochlorite, and so on. These reactions result in the generation of terminal oxidant adducts of the transition-metal catalysts, followed by conversion to high-valent metal oxo complexes that work as true reactive oxidants in the catalytic reactions. The structure and reactivity of the terminal oxidant adduct complexes and the high-valent metal oxo complexes have been studied in many groups.⁸⁻²⁷ Although the terminal oxidant adduct complexes are unstable compounds, there have been many reports of terminal oxidant adducts of hydrogen peroxide, ⁸⁻¹³ alkylperoxides, ^{14–16} and *m*-chloroperoxybenzoic acid. ^{17–20} In contrast to these successful reports, there have been only a few examples of hypochlorite adducts of metal complexes.²⁸⁻³⁰ Recently, we succeeded in the preparation and characterization of bis-hypochlorite and hypochlorite imidazole adducts of an iron(III) porphyrin complex for the first time.²⁸ More recently, hypochlorite adducts of nonheme nickel complexes were detected as precursors of high-valent nickel oxo species from the reactions of nickel(II) nonheme complexes with sodium hypochlorite.^{29,30} However, the binding structure and reactivity of metal-bound hypochlorite remain unclear. To address the structure and reactivity relationship of metal-bound hypochlorite, we report here the preparation, characterization, reactivity, and enantioselectivity of hypochlorite adducts of manganese(IV) salen complexes bearing a (R,R)-cyclohexane-1,2-diamine linkage as the chiral unit (Scheme 1).

Scheme 1. Synthesis of Manganese(IV) Bis-hypochlorite Complexes



We examined the preparation of the hypochlorite adduct of the manganese(IV) salen complex from the reactions of dichloromanganese(IV) salen complexes (1) with tetra-*n*butylammonium hypochlorite (TBA-OCl), which was prepared from tetra-*n*-butylammonium chloride and sodium hypochlorite in dichloromethane. Figure 1 shows the absorption spectral change for titration of the dichloromanganese(IV) salen complex having a *tert*-butyl group at the para position (1-^tBu) with TBA-OCl in dichloromethane at -20 °C. With the addition of TBA-OCl, the absorption spectrum of 1-^tBu changes to a new one



Figure 1. Absorption spectral change for the titration of 1-^tBu with TBA-OCl in dichloromethane at -20 °C: (blue line) 1-^tBu; (red line) 2-^tBu. Inset: EPR spectra of (a) 1-^tBu (blue line) and (b) 2-^tBu (red line) at 4 K.

Received: October 16, 2017

(2-^tBu) having absorption peaks at 350, 428, and 650 nm with clear isosbestic points. The titration of TBA-OCl indicates that 2 equiv of TBA-OCl is required for the formation of **2**-^t**Bu** (Figures 1 and S1), suggesting the formation of a bis-hypochlorite complex. Similar absorption spectral changes are obtained from the reactions of dichloromanganese(IV) salen complexes having chloro and nitro groups at the para position $(1-Cl \text{ or } 1-NO_2)$ with TBA-OCl (Figure S2). The broad strong absorption peak around 650 nm shows a blue shift as the electron-withdrawing effect of the para substituent of the salen ligand increases (2-Cl, 630 nm; 2-NO₂, 610 nm). These results indicate that this band is assignable to a ligand-to-metal charge-transfer band. To investigate the manganese oxidation state of 2-^tBu, we measured electron paramagnetic resonance (EPR) spectrum (Figure 1). The EPR spectrum of 2-^tBu in the perpendicular mode shows EPR signals at g = 4.93, 3.03, and 1.82, which are totally different from those of $1^{-t}Bu$, g = 5.43, 2.06, and 1.44.³¹ These EPR g values are typical of the $S = \frac{3}{2}$ spin state, suggesting a manganese(IV) oxidation state. The manganese(IV) oxidation state is further confirmed by the EPR measurement in the parallel mode (Figure S3), which does not show a significant EPR signal. The ¹H NMR spectrum of 2-^tBu showed paramagnetic NMR signals resulting from the phenolic protons of the salen ligand at -19.5 and -37.7 ppm from tetramethylsilane at -20 °C (Figure S4). These NMR shifts were close to those of manganese(IV) salen complexes reported in previous papers. ${}^{31-33}$ **2**- t **Bu** is stable for hours in dichloromethane under -20 °C but slowly decomposes to manganese(III) complexes over -20 °C. 2-^tBu can be isolated as a solid by the addition of excess cold hexane at -40 °C. The isolation of 2-^tBu was confirmed by its spectroscopic data (Figure S5). We tried to get a single crystal of 2-^tBu, but we failed to do so. To confirm the coordination of hypochlorite to the manganese(IV) center, we measured an IR spectrum of 2-^tBu (Figures 2 and S6). We found two sensitive



Figure 2. Difference spectrum ($^{16}O - {}^{18}O$) of the IR spectra (KBr) of ^{16}O - and ^{18}O -labeled 2-^tBu.

bands for the ¹⁸O isotope labeling of hypochlorite (¹⁸OCl⁻) at 473 and 725 cm⁻¹; these bands shifted to 455 and 696 cm⁻¹, respectively, for the ¹⁸O-isotope-labeled **2-**^t**Bu**. The observed ¹⁸O isotope shifts (18 and 29 cm⁻¹) are in good agreement with those (17 and 29 cm⁻¹) calculated for a triatomic O–Mn–O asymmetric stretching band and a diatomic O–Cl stretching band, respectively. We also performed ESI-MS analysis of **2-**^t**Bu** but could not obtain ion peaks corresponding to a hypochlorite

adduct (Figure S7). All of these spectroscopic characterizations indicate that **2-**^t**Bu** is a manganese(IV) bis-hypochlorite complex.

Conformation of $2^{-t}Bu$ in dichloromethane is investigated by means of circular dichroism (CD) spectroscopy. Previously, we reported that the intensity of the CD peak near 280 nm is a sensitive marker to estimate the conformation of the chiral manganese(IV) salen complex; the intensity of the band increases as the conformation of the salen ligand shifts from the planar conformation to the stepped conformation.^{31,32} The CD spectrum of $2^{-t}Bu$ showed weak CD bands at 326 and 275 nm (Figure S8), suggesting a planar conformation.

To investigate the reactivity of the manganese-bound hypochorite, we examined the reactions of 2-^tBu with various organic substrates. When thioanisole was added to 2-tBu, prepared from 1 and 2 equiv of TBA-OCl at -60 °C, the absorption spectrum of 2-^tBu quickly changed to that of 1-^tBu (Figure S9). Product analysis of the reaction showed the formation of phenvl methyl sulfoxide in 93% vield based on OCl-, showing that both of the manganese(IV)-bound hypochlorites are capable of oxygen-atom-transfer reaction to sulfide. We further examined the reactions of 2-^tBu with less reactive thioanisoles, *p*-chlorothioanisole and *p*-nitrothioanisole, at -60 °C. 2-^tBu oxidizes *p*-chlorothioanisole and *p*-nitrothioanisole to the corresponding sulfoxides in 60 and 50% yield based on OCl⁻ for 15 and 60 s at -60 °C, respectively, although TBA-OCl hardly oxidizes them under the same conditions (5% and 0%). Phenyl methyl sulfones, further oxidation products of phenyl methyl sulfoxides, are not detected in the present reactions. Moreover, we studied the reaction of 2-^tBu with thioanisole by EPR spectroscopy. The EPR spectrum of 2-^tBu completely changed to that of 1-^tBu in the perpendicular mode, but there were no significant EPR signals in the parallel mode immediately after the addition of 100 equiv of thioanisole (Figure S10). These results are consistent with the formation of 1-^tBu from the reactions of 1-^tBu with thioanisoles.

The nature of the manganese-bound hypochlorite is further studied by a Hammett plot analysis. The reaction processes of **2**-^t**Bu** with thioanisoles could be followed by rapid mixing stopped-flow experiments at -20 °C (Figures S11 and S12). The time courses of the absorbance for these reactions are simulated well with double-exponential functions, suggesting two successive sulfoxidation reactions (Scheme 2). Hammett plot analyses





show similar ρ values for these two processes ($\rho = -0.84$ and -0.92), indicating electrophilic character of the manganese(IV) bound hypochlorite. The estimated ρ values are smaller than those reported for the sulfoxidation reactions of various manganese(III) salen complexes with sodium hypochlorite ($\rho = -1.55$ to -2.38),³⁴ a nonheme oxomanganese(IV) complex ($\rho = -4.4$),³⁵ and oxomanganese(V) corrolazines ($\rho = -1.29$ to

We further examined the reactions of 2-^tBu with olefins to investigate the epoxidation reactivity. The absorption spectral change for the reaction of $2^{-t}Bu$ with *p*-methoxystyrene (1.0 M) at 25 °C is different from that with thioanisole at -60 °C (Figure S13). The absorption spectrum of the reaction product was not identical with that of 1-^tBu but a manganese(III) salen complex. This is further confirmed by EPR spectroscopy (Figure S14). As expected, the EPR signals resulting from 2-^tBu in the perpendicular mode become weak, and new EPR signals resulting from a manganese(III) complex in the parallel mode become strong after the addition of *p*-methoxystyrene for 2 h. Product analysis indicated the formation of *p*-methoxystyrene oxide in 48% yield based on OCl-, suggesting epoxidation reactivity of 2-^tBu. The reactions of 2-^tBu with other styrene derivatives under single-turnover conditions are summarized in Table 1. While *trans-\beta*-methylstryrene afforded *trans-\beta*-methyl-

Table 1. Reactivity and Enantioselectivity of Epoxidation Reactions by 2-^tBu

olefin	yield ^{a} (%)	ee (%)	ee of Jacobsen's catalyst (%) ^b
styrene	13	13	56	
<i>p</i> -methoxystyrene	48	nd	nd	
<i>cis-β</i> -methylstyrene	1 (cis)	25	85	
	5 (trans)	2	62	
<i>trans-β</i> -methylstyrene	36	3	20^{c}	
^{<i>a</i>} Yields are based or ^{<i>b</i>} Conditions: 4 °C for °C. ³²	n TBA-OC 3 h. ^c Reac	l. Cond tion wit	litions: 25 °C for 3 th iodosylmesitylene at 2	h. 25

stryene oxide, *cis-β*-methylstyrene produced a mixture of *cis-* and *trans-β*-methylstyrene oxides. These results suggest that the reactivity of $2^{-t}Bu$ to olefin is lower than that of a reactive species in the Jacobsen's reaction.³⁸⁻⁴⁰

We investigate the enantioselectivity of the epoxidation reactions of 2-^tBu in order to investigate its relationship to a reactive intermediate of Jacobsen's enantioselective epoxidation reactions (Figures S15 and S16).³⁸⁻⁴⁰ The results of the enantioselectivity are summarized in Table 1 by enantiomer excess (ee). The evalues of the epoxides produced by 2-^tBu under single-turnover reactions are much lower than those by Jacobsen's catalyst under catalytic conditions.^{38,39} The low enantioselectivity of 2-^tBu is consistent with the planar conformation of the salen ligand, as suggested by the present CD spectroscopy. 2-^tBu seems not to be a reactive intermediate in Jacobsen's enantioselective epoxidation reactions.

Kinetic (Hammett) analyses of the sulfoxidation reactions indicate that the rate-limiting step of the sulfoxidation reaction does not involve the O–Cl bond-cleavage step of the manganese(IV)-bound hypochlorite to form a high-valent oxo species but the direct reaction of $2^{-t}Bu$ with thioanisole. In addition, the absence of the isosbestic points and the kinetic traces simulated with double-exponential functions suggest a successive reaction mechanism (Scheme 2). The stoichiometric formation of $1^{-t}Bu$ also supports this mechanism. The epoxidation reactions are also induced by the direct reactions of $2^{-t}Bu$ with olefins. The absorption spectral change with an isosbestic point and the first-order reaction in the concentration of olefin for the epoxidation reaction ruled out the participation of the bond-cleavage process in the rate-limiting step (Figures S13 and S17). Formation of the manganese(III) species from the epoxidation reaction would result from thermal decomposition of the monohypochlorite complex formed after the first epoxidation reaction of $2^{-t}Bu$ with olefin because the decomposition reaction would be faster than the second epoxidation reaction at 25 °C. In fact, the epoxidation rate for the most reactive *p*-methoxystyrene is much smaller than the sulfoxidation rates and comparable to the decomposition rate of $2^{-t}Bu$ under concentrations of less than 0.1 M (Figures S12 and S17).

We further examined the chlorination and hydrogen abstraction reactions by **2-**^t**Bu**. **2-**^t**Bu** reacted with 1,3,5-trimethoxybenzene and 1,4-cyclohexadiene to afford 1-chloro-2,4,6-trimethoxybenzene and benzene in 20% yield at 0 °C and 40% yield at -20 °C based on OCl⁻, respectively. A detailed mechanistic study of these reactions is currently under investigation.

In summary, we have reported the preparation, characterization, and reactivity of a bis-hypochlorite adduct of a chiral manganese(IV) salen complex. The manganese(IV)-bound hypochlorite is capable of sulfoxidation, epoxidation, chlorination, and hydrogen abstraction, although the enantioselectivity is low.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02661.

Figures S1–S17 and experimental details (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was supported by grants from JSPS (Grants 25288032 and 17H03032), CREST, The Naito Foundation, and The Uehara Memorial Foundation. We thank IMS for assistance with EPR measurements.

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