金属锰 Corrole 的脱金属研究

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摘要: 合成了中位带有不同取代基的锰 corrole 配合物 **1**-Mn, **2**-Mn, **3**-Mn, **4**-Mn, 并研究了其酸解和还原脱金属特性。结果表明取代基的性质对脱金属产率有很大的影响。缺电子金属锰 corrole 的酸解脱金属产率比富电子金属锰 corrole 高, 而还原脱金属产率的顺序则正好相反。

关键词: 锰; corrole; 脱金属
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Demetalation of Manganese Corroles

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Abstract: Manganese (Ⅲ) corroles bearing different meso- substituents **1**-Mn, **2**-Mn, **3**-Mn, **4**-Mn have been synthesized and tested for the demetalation by using H_2SO_4/HAc and CH_2Cl_2 /$SnCl_2$(HCl) method. The demetalation yields depend on the substituents of corrole macrocycle significantly. Demetalation yield of electron-deficient Mn(Ⅲ) corrole is higher than electron-rich Mn(Ⅲ) corrole when using H_2SO_4/HAc method. But when using CH_2Cl_2 /$SnCl_2$ (HCl) reductive method, electron-rich Mn(Ⅲ) corrole gives higher demetalation yield.

Key words: manganese; corrole; demetalation

Corrole is an 18-π electron tetrapyyrolic macrocycle containing a direct pyrrole-pyrrole link. As a tri-anionic ligand with smaller cavity, corrole has the capacity to stabilize metals in high oxidation states[1]. Due to potential applications of manganese corroles in catalytic oxidation of organic substrates [2], artificial nuclease [3] and hydrogen atom transfer reaction [4], the study on manganese corroles has been developed very quickly in recent years[5]. Demetalation is a very important aspect

of metal corrole chemistry. In cases of porphyrin, new functionalized free base porphyrins may be prepared by demetalation strategy of metalloporphyrins[6]. However, the demetalation of metal corroles has not been received much attention, and no general procedures have been available so far. Broring et al.[7] reported that the demetalation of manganese β-octaethyl corrole went with high yield in HAc-HBr solvent. Quite recently, Paolesse et al. [8] found that dematalation of manganese corroles

might be achieved by CHCl₃/H₂SO₄ method. In our previous communication, we observed reductive demetalation of manganese corroles[9]. We report here the acid induced demetalation in H₂SO₄/Hac, as well as the reductive demetalation of manganese corroles and the substituent effects. Model manganese complexes selected are shown in scheme 1. To tune the electronic properties, these triaryl manganese(Ⅲ) corroles are designed to bear different numbers of pentafluorophenyl group at meso- positons.
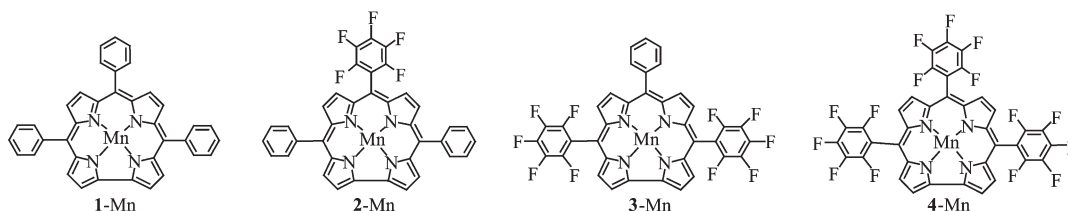
Scheme 1

1　Experimental

1.1　General

All chemicals were reagent grade and were used without further purification. ¹H-NMR spectra were recorded by a Varian 300 spectrometer. TMS in CDCl₃ was used as the reference for the chemical shift. ¹⁹F-NMR spectra were obtained by a Varian 300 spectrometer, operating at 282.4 MHz. UV-Vis spectra were recorded on a Varian cary 50 scan spectrophotometer. FAB-MS spectra were recorded by using Finigan 2000 spectrometer(Mode: +Q1MS; NBA matrix). Cyclic voltammetry was carried out on an IM6e electrochemical work station(Zahner, Germany) at room temperature. The counter, working and reference electrodes were Pt wire, graphite and Ag-AgNO₃ eletrode, respectively. The supporting electrolyte was tetrabutylammonium hexafluorophosphate(TBAPF₆)(0.1 mol·L⁻¹) and dichloromethane was utilized as the solvent.

1.2　Synthesis

5,10, 15-tris(phenyl)corrole(**1**): **1** was prepared according to the previously reported method[10].

5,15-bis(phenyl), 10-(pentafluorophenyl)corrole(**2**): 1 g 5-(phenyl)dipyrromethane (4.5 mmol) and 0.4 g pentafluorobenzaldehyde (2.0 mmol) were dissolved in 250 mL dried dichloromethane. 50 μL trifluoroacetic acid(TFA)was then added and the reaction mixture was stirring at room temperature for 6 h. The reaction was quenched by adding 100 μL triethylamine. 0.5 g 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was added and allowed to stir for 1 h. Final product was purified by chromatography on silica gel by using hexane/CH₂Cl₂ (1:4, V/V) as eluant. 110 mg 2 was obtained with a yield of 8.9%. FAB-MS: m/z 616(M⁺, 100%); ¹H NMR(in CDCl₃): δ ppm, 8.96(d, 2H), 8.87(br, 4H), 8.80(d, 2H), 8.23 (m, 4H), 7.80 (m 6H); ¹⁹F NMR (in CDCl₃): δ ppm, −138.2(2d, 2F), −154.0(t, 1F), −162.6(m, 2F). UV-Vis(in CH₂Cl₂): λ_{max}(relative intensity), 412.7 nm(0.96), 574.3 nm (0.16).

5,15-bis(pentafluorophenyl), 10-(phenyl)corrole (**3**): 0.8 g 5-(pentafluorophenyl)dipyrromethane (2.6 mmol) and 0.13 g pentafluorobenzaldehyde (1.2 mmol) were dissolved in 250 mL dried dichloromethane. 50 μL TFA was then added and the reaction mixture was stirring at room temperature for 6 hours. The reaction was quenched by adding 100 μL triethylamine. 0.5 g DDQ was added and allowed to stir for 1 h. Final product was purified by chromatography on silica gel by using hexane/CH₂Cl₂ as eluant(1:4, V/V). 90 mg 3 was obtained with a yield of 10.6%. FAB-MS: m/z 706(M⁺,100%); ¹H NMR(in CDCl₃): δ ppm, 9.11(d, 2H), 8.69(s, 4H), 8.56 (d, 2H), 8.16(m, 2H), 7.75(m 3H); ¹⁹F NMR(in CDCl₃): δ ppm, −138.3 (2d, 4F), −153.2 (t, 2F), −162.1 (m, 4F). UV-Vis (in CH₂Cl₂): λ_{max} (relative intensity), 409.7 nm (1.09), 562.5 nm(0.18), 612.8 nm(0.11).

5, 10, 15-tris (pentafluorophenyl)corrole (**4**): **4** was prepared as previously reported[11].

Mn corrole: MnⅢ corrole was prepared by refluxing the mixture of free base corrole and Mn(AcO)₂·4H₂O (molar ratio: 1:10) in methanol for 2 h, and then the product was purified by chromatograph on silical gel using dichloromethane as eluant.

1.3　General procedures for demetalation

　　HAc-H₂SO₄ method: 10 mg manganese corrole was dissolved in 4 mL concentrated H_2SO_4/HAc (V/V, 1/3), the reaction was carried out at 40 ℃ under stirring for 2 d. The reaction mixture was poured into 20 mL ice water and was extracted by CH_2Cl_2(20 mL×3). The organic layer was washed twice with an aqueous $NaHCO_3$ solution and dried over sodium sulfate. CH_2Cl_2 was removed by distillation. Chromatography on silica gel (eluant: CH_2Cl_2/Hexane 1:1, V/V) to afford corresponding free base corrole.

　　Reductive demetalation method: 10 mg manganese corrole was dissolved in 25 mL CH_2Cl_2 in a 50 mL flask, to the solution 6 mL concentrated hydrochloric acid and 42.5 mg $SnCl_2·2H_2O$(0.19 mmol) were added, the mixture was then refluxed at 40 ℃ under stirring for 2 d. After reaction mixture cooling down to room temperature, the organic layer was separated and washed twice with saturated Na_2HCO_3 solution, CH_2Cl_2 was removed by distillation, the product was purified by chromatograhpy on silica gel with CH_2Cl_2/Hexane(1:1, V/V) as eluant.

2　Results and discussion

　　In order to investigate the substituent effect on the demetalation propeties, manganese(Ⅲ) corroles bearing different number of pentafluorophenyl groups at mesopositions were chosen as model complexes(scheme 1). All synthesized free base corroles exhibited similar UV-Vis spectra. And with the increasing of pentafluorophenyl groups, the Soret and Q band of free base corrole are blue shifted slightly(Fig.1). The blue shift may be explained by the increase of the energy gap between the HOMOs and LUMOs of free base corroles, which is induced by electron-withdrawing groups[2b]. The electronic spectra of corresponding manganese(Ⅲ) corroles are also sensitive to the substituents, especially the relative intensity and the wavelength number of the right arm of Soret bands(Fig.2). It is noteworthy that manganese(Ⅲ) 5,10,15- tris(phenyl)corrole 1-Mn is not stable in CH_2Cl_2 solution, it will slowly turn into manganese(Ⅳ) corrole as indicated by the UV-Vis spectra and the colour changes from green to brown.
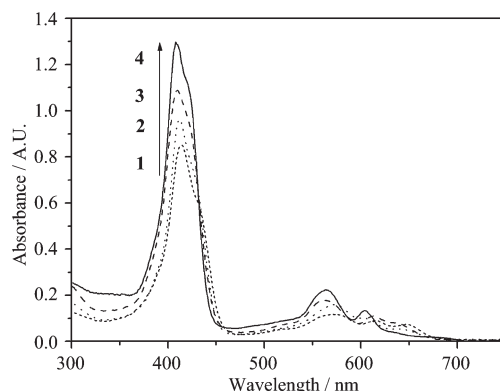

Fig.1　UV-Vis spectra of free base corrole **1**, **2**, **3**, **4** in CH_2Cl_2
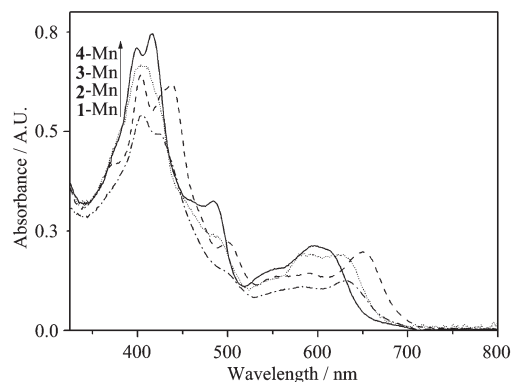

Fig.2　UV-Vis spectra of manganese(Ⅲ) corrole **1**-Mn, **2**-Mn, **3**-Mn, **4**-Mn in CH_2Cl_2

　　We have also examined the electrochemistry of **1**-Mn, **2**-Mn, **3**-Mn and **4**-Mn. The cyclic voltammograms of **1**-Mn, **2**-Mn, **3**-Mn and **4**-Mn in CH_2Cl_2 are shown in Fig.3. Two one-electron oxidations can be observed for **1**-Mn and **2**-Mn. Based on the previous electrochemistry study of manganese corrole by Kadish[12], the first reversible one-electron oxidations of **1**-Mn ($E_{1/2}$=0.04 V) and **2**-Mn($E_{1/2}$=0.20) are assigned as Mn(Ⅲ)/Mn(Ⅳ) couple. And the second one-electron oxidations of **1**-Mn ($E_{1/2}$=0.76 V) and **2**-Mn($E_{1/2}$=0.88 V) may be assigned as the oxidation of corrole macrocycle to give π-cation radicals. For more electron-deficient manganese corrole **3**-Mn and **4**-Mn, $E_{1/2}$ of Mn(Ⅲ)/Mn(Ⅳ) couple is 0.31 V and 0.48 V, respectively. And the corrole macrocycle oxidation peak of **3**-Mn and **4**-Mn could not be observed within the given frame of electrochemical window. Generally, the Mn(Ⅲ)/Mn(Ⅳ) couple is not observable by electrochemical reduction of Mn(Ⅲ) corrole, it will result in the formation of corresponding π-anion radicals[12]. $E_{1/2}$
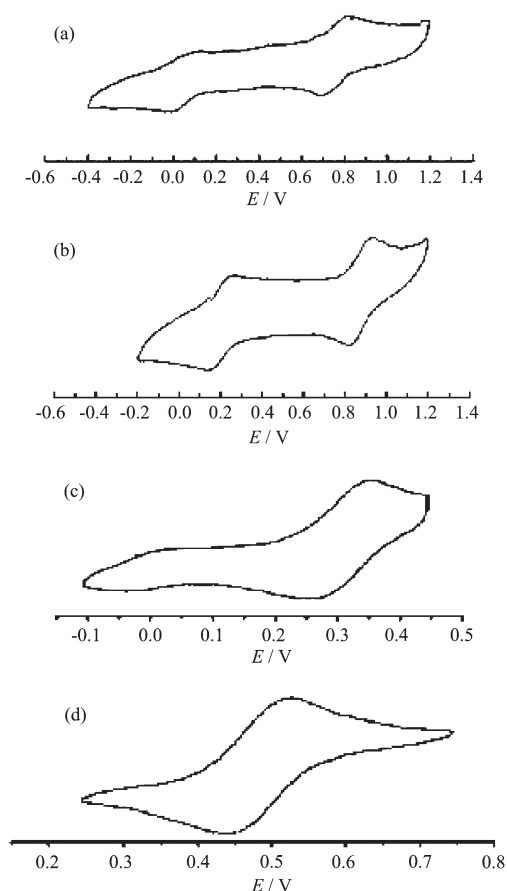
Fig.3　Cyclic voltammogram curves of four manganese(Ⅲ)-corroles: (a) **1**-Mn；(b) **2**-Mn；(c) **3**-Mn；(d) **4**-Mn; Solvent: CH_2Cl_2, 0.1 mol·L^{-1} TBAPF6; Scan rate= 0.1 V·s^{-1}; Electrode: Graphite/Pt/Ag-AgNO_3 (working/counter/reference electrode)

of Mn(Ⅲ)/Mn(Ⅳ) couple follows an order of **4**-Mn>**3**-Mn>**2**-Mn>**1**-Mn. It can be seen that the redox potential of central manganese ion moves positively with the increasing of meso- pentafluorophenyl.

The first example of demetalation of manganese corrole was reported by Broring[7], in which they used HBr/HAc as solvent and it was quite effective for demetalation of β-substituted manganese corrole. When we used the same method for demetalation of manganese(Ⅲ) 5, 10, 15-tris(pentafluorophenyl)corrole Mn^{Ⅲ} TPFC, it was found that only little free base 5, 10, 15-tris(pentafluorophenyl)corrole(TPFC) could be isolated and significant β-brominated products mixture was formed as identified by MS. The demataltion of manganese porphyrins is often carried out in H_2SO_4/HAc mixed solvent[13]. So we tried this method for the demetalation of manhanese corroles, and demetalation of manganese corroles could also be observed by H_2SO_4/HAc methods with less byproduct. To optimize the reaction conditions, demetalation of **4**-Mn was tested at different ratios of H_2SO_4/HAc and the results are listed in table 1. From table 1, it can be seen that the best H_2SO_4/HAc volume proportion for demetalation of **4**-Mn is 1∶3 (V/V). The effects of temperature and reaction time on the demetalation yields of **4**-Mn are listed in table 2. The optimized demetalation reaction condition is to keep the reaction at 40 ℃ for two days in H_2SO_4/HAc(V/V, 1/3). It should be pointed out that, while we are preparing this manuscript, Paolesse et al.[8] reported a $CHCl_3$/H_2SO_4 method, which is also effective for the demetalation of manganese corroles.

By using H_2SO_4/HAc method, the isolated demetalation yields of **1**-Mn, **2**-Mn, **3**-Mn, **4**-Mn at optimized conditions are 28.5%, 31.6%, 53.7% and 67.0%, respectively. This is contrary to the expectation for acid-induced demetalation. Since in Mn(Ⅱ) porphyrin cases[14], the higher the basicity of pyrrolic

Table 1　Effect of H_2SO_4/HAc volume proportion on demetallation yield of 4-Mn^a

$V_{H_2SO_4}$ / V_{HAc}	1/5	1/4	1/3.5	1/3	1/2.5	1/2	1/1	H_2SO_4
Yield / %	10.6	23.4	42.6	67.0	40.5	38.3	7.4	18.1

a: Reaction was carried out at 40 ℃ for 2 d.

**Table 2　Effects of reaction temperature and time on the demetallation yield of 4-Mn^a**

	Time / d^b						Temp.			
	0.5	1.0	1.5	2.0	2.5	3.0	30.0	40.0	50.0	60.0
Yield (%)	27.7	36.2	51.1	67.0	54.2	42.1	21.3	67.0	23.4	12.8

a: HAc/H_2SO_4, V/V=3:1; b: Temp., 40 ℃

nitrogen atoms is, the easier the Mn(II) porphyrins undergo demetalation. The nitrogen atoms basicity of electron-rich corrole is higher than electron-deficient corrole, so **1**-Mn is expected to have the largest acid-induced demetalation yield among these four manganese corroles. The observed results can be explained by the fact that electron-rich Mn(III) corroles will quickly turn into Mn(IV)corroles in H_2SO_4/HAc solutions. And Mn(IV) corrole is stronger in resisting acid-induced dematalation. This may be confirmed by testing the demetalation of Mn^{III} TPFC(**4**-Mn) and its Mn(IV) complex Mn^{IV} TPFC. Under the optimized conditions, the isolated acid-induced demetalation yield drops from 67.0% of Mn^{III} TPFC to 29.3% of Mn^{IV} TPFC.

The demetalation of manganese corroles could also be achieved by reductive method in CH_2Cl_2 with $SnCl_2$ (in concentrated aqueous HCl). By using CH_2Cl_2/$SnCl_2$ (HCl) method described in experimental section, the isolated demetalation yields of **1**-Mn, **2**-Mn, **3**-Mn, **4**-Mn are 46.6%, 41.1%, 29.0% and 10.7%, respectively. It has been reported that reductive demetalation of silver(II) corrole could be achieved in CH_2Cl_2 or $CHCl_3$/HCl(aqueous) biphasic system [15]. This method doesnt

work for the demetalation of manganese corroles. In this system, **1**-Mn, **2**-Mn, **3**-Mn, **4**-Mn would turn from manganese(III) into manganese(IV) corroles and no demetalation could be observed. This indicates that $SnCl_2$ plays a key role in the demetalation. That is, this is a reductive demetalation processes. Interestingly, demetalation yields of **1**-Mn, **2**-Mn, **3**-Mn, **4**-Mn are quite different, varying from 46.6% of 1-Mn to 10.7% of **4**-Mn. It follows an order of **1**-Mn >**2**-Mn >**3**-Mn >**4**-Mn, showing electron-rich manganese corroles undergo easier reductive demetalations than those electron-deficient ones. This is in good accordance with the expected reductive demetalation yield order of these manganese corroles. For the $E_{1/2}$ of Mn(III)/Mn(IV) couple follows an order of **4**-Mn>**3**-Mn>**2**-Mn>**1**-Mn as mentioned above. It is known that Mn(II) porphyrin is unstable in acidic solvent, it would demetaled even if in weak acid solution [16]. The reductive demetalation of manganese corroles in prsent system may also be involved a Mn(II) corrole species(scheme 2). The key step is the reduction of central Mn(III) to Mn(II) ion, then Mn(II) corrole would undergo acid induced demetalation via the protonation of pyrrolic nitrogen atoms.
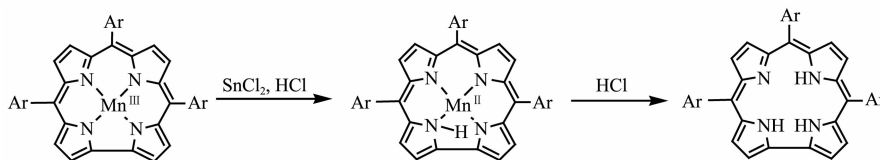
scheme 2

3　Conclusions

　　Manganese (III) corroles bearing different meso-substituents **1**-Mn, **2**-Mn, **3**-Mn, **4**-Mn have been synthesized and tested for the demetalation by H_2SO_4/ HAc and CH_2Cl_2/$SnCl_2$(HCl) method. It is found that meso-substituents have strong effects on the demetalation of manganese corroles. When using acid-induced demetalation in H_2SO_4/HAc solvent, the demetalation yield of electron-deficient Mn(III) corrole is higher than electron-rich Mn(III) corrole, because the later is easier oxidized to Mn(IV) corrole under acidic conditions. However, when using CH_2Cl_2/$SnCl_2$(HCl) reductive demetalation method, electron-rich Mn (III) corrole gives higher demetalation

yield. Because Mn(III) ion in electron-deficient Mn(III) corrole has more positive redox potential, it is more difficult to be reduced by $SnCl_2$.

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