Asian Journal of Chemistry; Vol. 26, No. 20 (2014), 7052-7054

ASIAN JOURNAL OF CHEMISTRY

<http://dx.doi.org/10.14233/ajchem.2014.17961>

Synthesis and Characterizations of Maleate Complex with Iron of Variable Valence

YAN ZHENG¹ and JIANBIN ZHANG^{2,*}

¹Department of Chemical Engineering, Inner Mongolia Vocational College of Chemical Engineering, Huhhot 010070, P.R. China

²College of Chemical Engineering, Inner Mongolia University of Technology, Huhhot 010051, P.R. China

*Corresponding author: Tel/Fax: +86 471 6575722; E-mail: tadzhang@pku.edu.cn; 10510892@pku.edu.cn

Received: 7 May 2014;

Accepted: 10 July 2014;

Published online: 25 September 2014;

AJC-16065

In this work, the ferrous maleate complexes of $\text{Fe}(\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ were synthesized by three ways, including the reaction of maleic acid ($\text{C}_4\text{H}_4\text{O}_4$) with the ferrous carbonate (FeCO_3) in aqueous solution, the reaction of ammonium maleate solution with ferrous dichloride (FeCl_2) and the reaction of maleic acid with iron powders at 40–50 °C. The structural and compositional investigations of the complexes were performed by Fourier transform infrared, thermogravimetry and derivative thermogravimetry and elemental analysis techniques.

Keywords: Maleic acid, Maleic anhydride, Metal complex, Polymaleic anhydride.

INTRODUCTION

The C=C double bond of unsaturated fatty chain in α,ω -dicarboxylic acid restricts the carbon chain to rotate freely reducing its conformational degrees of freedom, which makes α,ω -dicarboxylic acid coordinate with other ligands hardly¹. Because of the lowest carbon acid in the series of unsaturated α,ω -dicarboxylic acid, *cis*- and *trans*-butanedioic acid have their particularity in the construction of complexes. *cis*- and *trans*-Butanedioic acid are used as bridging ligand to synthesize other complexes rarely results from their low dissolubility in inorganic solvents². However, carboxylic-terminated *cis*- and *trans*-butanedioic acid are the potential multidentate ligands to synthesize metal complex used as polymeric monomer to synthesize many valuable polymerization products. Furthermore, the metal complex is also a valuable magnetic material because of the π electron in the double bond, which could provide the opportunity for the magnetic coupling³.

The presence of the ionic bond and unsaturated double bond, unsaturated carboxylic acid metal complex could appear homopolymerization and grafting cross-linking with the matrix material, which increase the chemical and physical cross-linking in the conjugate. The dual cross-linking of unsaturated carboxylic acid metal complex could improve the strength and toughness of vulcanizate greatly compared with the traditional reinforcing agent⁴. In addition, the adhesion property of the matrix and skeleton material could be improved significantly in the presence of metal ion in unsaturated carboxylic acid metal complex⁵. Therefore, the metal salt of unsaturated

carboxylic acid is a kind of promising multifunctional additive in the field of polymer materials because of excellent cross-linking, reinforcing and adhesive properties and could be used in the field of rubber, plastic and fiber widely⁶.

The complexes of transition metal with carboxylic acid ligands have been draw attention in molecular devices, fluorescence and magnetic fields and the complexes of metal maleic acid have been extensively studied⁷. However, the metal complexes of iron ion of variable valence with maleic acid have not been reported in the previous work. In this work, the ferrous maleate complexes were synthesized and the structural and compositional investigations of the complexes were performed by Fourier transform infrared, thermogravimetry and derivative thermogravimetry and elemental analysis techniques.

EXPERIMENTAL

FTIR spectra were recorded on a Bruker VECTOR22 spectrometer with 1 cm^{-1} resolution in the range from (4000–400) cm^{-1} using KBr pellets. The spectrometer possesses autoalign energy optimization and a dynamically aligned interferometer, an OPUS/IR operator and IR source. Elemental analysis on Perkin Elmer 2400 CHN elemental analyzer. Thermogravimetric analysis was performed using a derivatograph Q-1500D (MOM, Hungary) with simultaneous recording of TG and DTG curves in relation to temperature and time (heating rate: 10°C/min, temperature range: 20–600 °C). All the chemicals used in this study were of analytical-grade. All working solutions of desired concentrations were obtained

by diluting the stock solution with distilled water and prepared by mass using an analytical balance (Sartorius BS 224S) with ± 0.0001 g accuracy.

General procedure: Ferrous carbonate was synthesized using sodium carbonate and ferric sulfate. The superfluous maleic acid solution (2 mmol) was added into the precipitation of ferrous carbonate by dropping at room temperature for 1 h. Then the reaction mixture was filtered and the filter liquor was placed in shadow indoors for a week to ensure the solvent evaporate completely and the yellow crystal was obtained. The obtained yellow crystal was washed several times using tetrahydrofuran to remove the unreacted maleic acid. After that, the coarse crystals were recrystallized for many times to obtain the high purity yellow product in 17.80 % yield. The crystal was found to be readily soluble in water and scarcely soluble in acetone and tetrahydrofuran.

Ammonia was added into 2 mmol maleic acid solution until the pH value was about 6-7 to prepare ammonium maleate solution. Then 1 mmol aqueous solution of ferrous chloride was introduced into ammonium maleate solution quickly and the reaction mixture was stirred for 1 h at room temperature under nitrogen. Then the reaction mixture was filtered and the pH value of the filter liquor was adjusted to 2. After that, the filter liquor was placed in shadow indoors for a week to ensure the solvent evaporate completely and the yellow crystal was obtained. The coarse crystals were recrystallized for many times to obtain the high purity yellow product in 15.26 % yield. It was found that the crystal is readily soluble in water and scarcely soluble in acetone and tetrahydrofuran.

0.5 mmol micro-iron powder was introduced into 1 mmol aqueous solution of maleic acid and the reaction mixture was stirred for 5 h at room temperature under nitrogen atmosphere. Then the reaction mixture was filtrated and the filter liquor was placed in shadow indoors for 24 h, then the yellow crystal was precipitated. The coarse crystals were recrystallized for many times to obtain the high purity yellow product in 20.63 % yield. The crystal was readily soluble in water and scarcely soluble in acetone and tetrahydrofuran.

RESULTS AND DISCUSSION

The carbon and hydrogen content of the three synthesized crystals were determined by elemental analyzer and iron content was determined by phenanthroline spectrophotometric method. The results are showed in Table-1. From Table-1, it is found that the carbon, hydrogen and iron content in three crystals are similar, which agree reasonably well with the corresponding theoretical element contents of 26.81, 3.91 and 15.64 wt. % in $\text{Fe}(\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$. The results reveal that the obtained products in the three synthetic methods are the same crystal and the molecular formula is $\text{Fe}(\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$.

The recorded FTIR spectra of maleic acid and ferrous maleate complex are shown in Fig. 1. It is found that a broad and strong peak appear at 3385.49 cm^{-1} in ferrous maleate complex, which is attributed to the stretching vibrational band of hydroxyl in the four water molecules of complexes⁸. In ferrous maleate complex, the bands located at 1562.45 and 1480.51 cm^{-1} were asymmetry stretching vibration $\nu_{\text{as}}(\text{OCO})$ and the stretching vibration $\nu_{\text{s}}(\text{OCO})$ of carboxyl, respectively⁹

TABLE-1
CARBON (C), HYDROGEN (H) AND IRON
(Fe) CONTENT IN THREE CRYSTALS

Crystals	C (wt. %)	H (wt. %)	Fe (wt. %)
I	26.91	3.624	15.46
II	27.16	3.742	15.60
III	26.96	3.850	15.49

Fig. 1. FTIR spectra of maleic acid (above) and ferrous maleate complex (below)

and their difference value is 81.94 cm^{-1} . The carboxyl of maleic acid could coordinate with ferrous in the forms of monodentate, bidentate and bridged coordination¹⁰. In monodentate coordination, the asymmetry stretching vibration and the stretching vibration bonds of carboxyl shift to higher wave number and lower wave number, respectively and their difference value of peak position is more than 200 cm^{-1} . In bidentate coordination, the bonds shift to lower wave number and higher wave number, respectively and their difference value of peak position is in the rang of $40\text{-}80 \text{ cm}^{-1}$. In bridged coordination, their difference value of peak position is about 140 cm^{-1} ¹¹. Accordingly, we present that the maleic acid coordinate with ferrous atom in the form of bidentate coordination as following:

Fig. 2 gives the results from TG and DTG analysis carried out on ferrous maleate complex. It was found that the decomposition of the complex takes place in two stages. The first stage, which occurs at temperatures ranging from $100\text{-}153^\circ\text{C}$ involves the loss of four crystal water molecules presenting in the sample of $\text{Fe}(\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ with approximately the weight loss of 20.76 wt. %, which agree well with the theoretical content (20.11 wt. %). The second weight loss step occurring at $160\text{-}380^\circ\text{C}$ is related to the decomposition of skeleton fracture of maleic anhydride in the sample with approximately the weight loss of 56.88 wt. %, which coincide well with the theoretical content (57.54 wt. %). The total weight loss is 77.64 wt. % and the residual quantity is 22.36 wt. % coinciding well with the theoretical content of residual iron oxide (22.34 wt. %). The above thermal characteristic is similar with the typical carboxylic acid complex¹²⁻¹⁵. The thermogravimetric results prove the correctness of the elemental and FTIR spectral analysis.

Fig. 2. TG and DTG curves of ferrous maleate complex

Conclusion

In this work, the three ferrous maleate complexes were synthesized by the reactions of maleic acid with the ferrous carbonate, ammonium maleate solution with ferrous dichloride and maleic acid with iron powders, respectively. Meanwhile, the structural and compositional of the complexes were investi-

gated by FTIR, TG/DTG and elemental analysis techniques. The results show that the synthesized complexes are the same crystal of $\text{Fe}(\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ and the maleic acid coordinate with ferrous atom in the form of bidentate coordination.

REFERENCES

1. H.Y. Liu, J.J. Huang, B. Peng, G.T. Luo, Y.Y. Yang and L.N. Ji, *Wuji Huaxue Xuebao*, **1**, 652 (1997).
2. R. Shoji, T. Takeuchi and I. Kubo, *Anal. Chem.*, **75**, 4882 (2003).
3. J.B. Zhang, P.Y. Zhang, G.H. Chen, F. Han and X.H. Wei, *Prog. Chem.*, **4**, 771 (2009).
4. Y. Meng, Z. Wei, Y. L. Lu and L.Q. Zhang, *EXPRESS Polym. Lett.*, **6**, 882 (2012).
5. L.J. Boucher and J.J. Katz, *J. Am. Chem. Soc.*, **87**, 1340 (1967).
6. A. Kumar, *Tetrahedron Lett.*, **48**, 7278 (2007).
7. R. Lucas, J. Vergnaud, K. Teste, R. Zerrouki, V. Sol and P. Krausz, *Tetrahedron Lett.*, **49**, 5537 (2008).
8. C.C. Guo, *Org. Chem.*, **4**, 416 (1991).
9. D.Q. An, *Spectrosc. Spect. Anal.*, **21**, 478 (2001).
10. J. Yu, *Spectrosc. Spect. Anal.*, **24**, 981 (2004).
12. M. Lan, H. Zhao, H. Yuan, C. Jiang, S. Zuo and Y. Jiang, *Dyes Pigments*, **74**, 357 (2007).
13. L.Z. Wang, *Spectrosc. Spect. Anal.*, **28**, 2312 (2008).
14. H. Dehghani and F. Fathi, *Dyes Pigments*, **77**, 323 (2008).
15. H. Chiniforoshan, N. Safari, J.M. Nezhad, H. Hadadzadeh and A.H. Mahmoudkhani, *Inorg. Chim. Acta*, **359**, 2101 (2006).