

Oxidic Systems from Some Organometallic Precursors

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Abstract

The oxidation of ethylene glycol with Co(II), Ni(II) and Fe(III) nitrates in dilute acid solutions was investigated. The Co(II)/Fe(III) and Ni(II)/Fe(III) heteropolynuclear coordination compounds, having as ligand the oxidation product of ethylene glycol, were both prepared. Under specific working conditions, the oxidation of ethylene glycol to glyoxylic acid takes place, which is coordinated to Ni(II), Co(II) and Fe(III) cations as glyoxylate anion ($C_2H_2O_4^{2-}$), with simultaneous isolation of the corresponding heteropolynuclear coordination compound in both cases. The semi-empirical (PM7) structural investigations of the monomeric units and the thermal analysis (TG, DTG and DSC) of the heteropolynuclear coordination compounds, which are precursors of mixed oxides, are briefly presented.

Introduction

In our previous papers [1-10], the results of the oxidation of 1,2-ethanediol (ethylene glycol, EG), 1,2-propanediol and 1,3-propanediol with metal nitrates have been described. The complex compounds obtained by this original method contain glyoxylate, oxalate, lactate and 3-hydroxypropionate anions as ligands. The thermal conversion of homo- and heteropolynuclear coordination compounds with carboxylic acid anions as ligands has been carried out, producing metal oxide systems with irreducible structure and properties, which are required by today's technology in different fields: catalysis, electrocatalysis, pigments, electronics, supports for information storage and processing, and also drug industry [11-13]. These coordination compounds undergo thermolysis at relatively low temperatures, giving oxides and gaseous byproducts. The thermal decomposition of solid heteropolynuclear coordination compounds has also been used in the last years for the synthesis of nanoferrites. This method offers the possibility of controlling the composition and microstructure of the final product by selecting suitable ligands. The spinel ferrites and the mixed oxides of spinel type in general show great promise in modern electronic technologies as microwave absorbers, chemical sensors and catalysts, and also in biomedical applications. The fine particle nature of the ferrite, achieved by soft chemistry synthesis methods, is crucial for all these applications [14,15].

This paper shows the results obtained during investigation of EG's oxidation with cobalt(II), nickel(II) and iron(III) nitrates, using an acidic aqueous medium ($pH \approx 1 \div 2$). The obtained coordination compounds, namely $[CoFe_2(C_2H_2O_4)_2(OH_2)_6O_2]_n \cdot 1.5nH_2O$ and $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]_n \cdot 1.5nH_2O$, were studied regarding their composition and physical-chemical properties. It was shown that they can also act as precursors for nickel ferrite ($NiFe_2O_4$) and cobalt ferrite ($CoFe_2O_4$) which can thus be obtained at relatively low temperatures.

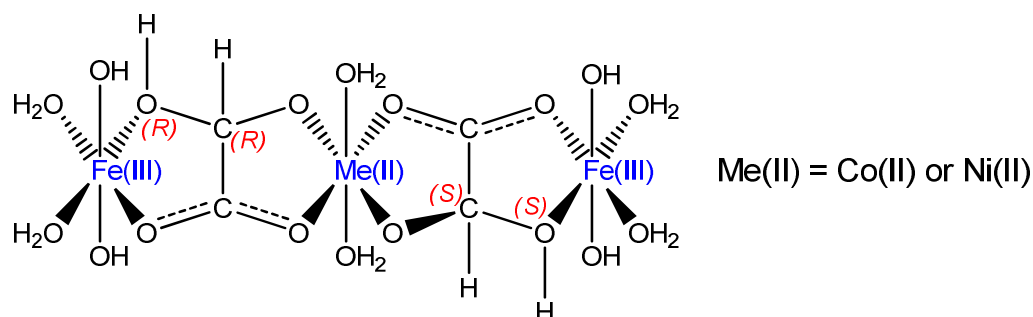
Experimental

As starting materials, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, aqueous nitric acid and EG were employed. The impurities from the reagents are removed in the subsequent purification step of the coordination compound. TG, DTG and DSC curves (in the 25–1000°C range), were registered on a Netzsch Simultaneous TG-DTA/DSC 409PC instrument using a 10 K min^{-1} heating rate, in both static air and inert (argon) atmospheres.

Both monomeric structures were drawn using the *HyperChem* molecular modeling software. After the “Add H & Model Build” command, the starting molecules were pre-optimized with the “MM+” force field (“Polak-Ribière” algorithm, RMS gradient of $0.01 \text{ kcal}/(\text{\AA} \text{ mol})$). *MOPAC 2012* software was subsequently used for the PM7 semi-empirical optimization. The line of parameters included “CHARGE=0”, “PM7”, “GNORM=0.01”, “UHF”, “OPT”, “BONDS”, “AUX”, “GRAPHF” and “PDBOUT”. The keyword “SINGLET” was used for the nickel compound, and “DOUBLET” for the cobalt compound. The data sets were obtained by using both the “EF” and the “BFGS” algorithms. The resulting structures were analyzed using the *Jmol* software. PM3 data are also given for comparison.

Results and discussion

The physical-chemical analyses (electronic spectroscopy, FTIR, XRD) performed have suggested that the monomeric unit should have the following structure for both heteropolynuclear coordination compounds (the *R/S* configurations were randomly chosen for the molecular modeling experiments):



Some parameters obtained through molecular modeling are given in Table 1.

Table 1. Heat of formation values for the monomeric units

Structure	$\Delta_f H$ (kcal/mol)		
	PM3	PM7 BFGS	EF
Cobalt compound	-1779.7	-974.7	-977.0
Nickel compound	-1774.6	-1016.9	-1018.5

The molecular models for both monomeric units are shown in Figure 1.

In order to show that $[\text{CoFe}_2(\text{C}_2\text{H}_2\text{O}_4)_2(\text{OH}_2)_6\text{O}_2]_n \cdot 1.5n\text{H}_2\text{O}$ is decomposed to CoFe_2O_4 , the thermal analysis methods were invoked. The obtained TG curves, in air and, respectively, in argon, shown in Figure 2, suggest six steps that take place at the progressive heating of this compound (temperature intervals given for the aerobic decomposition):

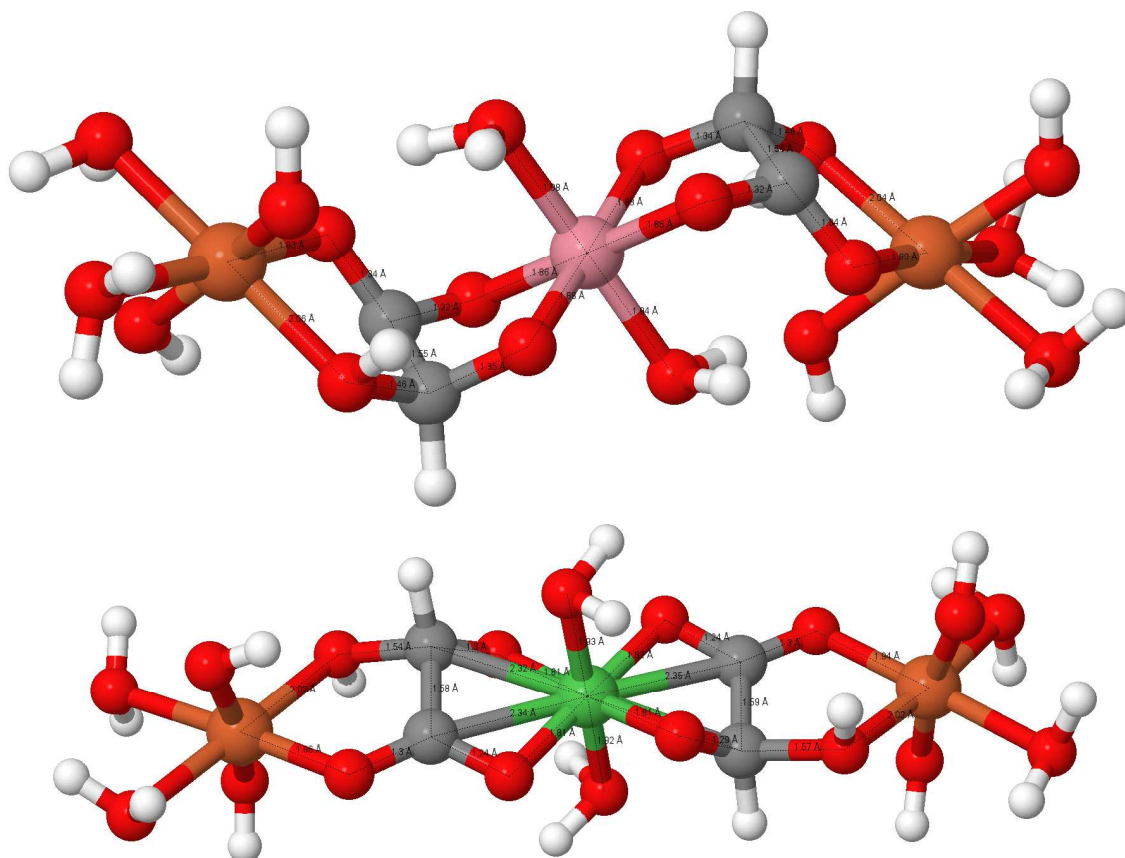


Figure 1. Monomeric units (BFGS) of cobalt (left) and nickel (right) coordination compounds

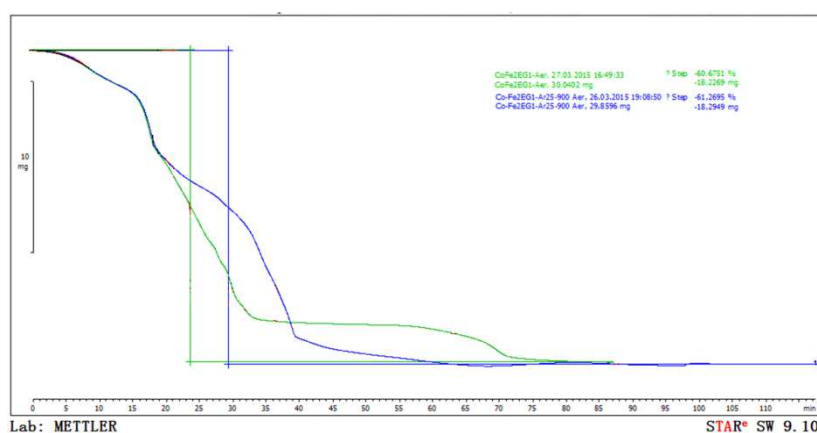
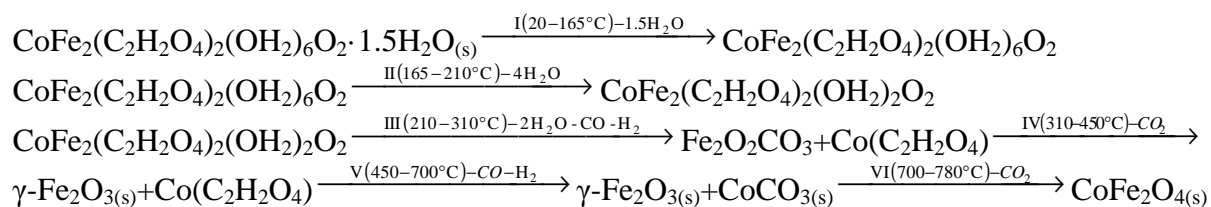
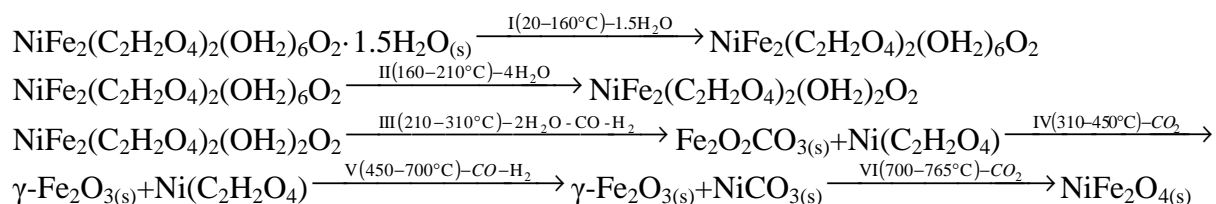


Figure 2. TG curves for the decomposition in air (green) and argon (blue) of $[\text{CoFe}_2(\text{C}_2\text{H}_2\text{O}_4)_2(\text{OH}_2)_6\text{O}_2]_n \cdot 1.5n\text{H}_2\text{O}$

The CoFe_2O_4 spinel, obtained at 780°C , is the final product of the conversion of the $[\text{CoFe}_2(\text{C}_2\text{H}_2\text{O}_4)_2(\text{OH}_2)_6\text{O}_2]_n \cdot 1.5n\text{H}_2\text{O}$ complex compound,

Similarly, in order to establish the conditions under which the $[\text{NiFe}_2(\text{C}_2\text{H}_2\text{O}_4)_2(\text{OH}_2)_6\text{O}_2]_n \cdot 1.5n\text{H}_2\text{O}_n$ complex compound is decomposed to NiFe_2O_4 , the thermal analysis methods were also used. The obtained thermograms again suggest six main steps to occur during the aerobic heating of this coordination compound:



The NiFe_2O_4 spinel, produced at 765°C , is the final product of the conversion of the $[\text{NiFe}_2(\text{C}_2\text{H}_2\text{O}_4)_2(\text{OH}_2)_4\text{O}_2]_n \cdot 1.5n\text{H}_2\text{O}$ coordination compound.

Conclusion

A new method for the synthesis of coordination compounds having the glyoxylate anion as ligand consists in the oxidation of EG in a diol-water system by nickel nitrate or cobalt nitrate, iron nitrate and nitric acid, with the simultaneous isolation of the corresponding complex compounds in the reaction system. The coordination compounds synthesized by this new method are heteropolynuclear combinations with the formula $[\text{M}^{\text{II}}\text{Fe}_2(\text{C}_2\text{H}_2\text{O}_4)_2(\text{OH}_2)_6\text{O}_2]_n \cdot 1.5n\text{H}_2\text{O}$ ($\text{M} = \text{Co}$ or Ni). These compounds were investigated by thermal analysis (TG, DTG and DSC) and quantum chemistry (PM7) methods. The mixed spinels $\text{M}^{\text{II}}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Co}$ or Ni) obtained by thermal decomposition of these heteropolynuclear coordination compounds are the main components of their conversion.

References

- [1] M. Niculescu, N. Vaszilcsin, M. Birzescu, P. Budrueac, E. Segal, J. Therm. Anal. Cal., 63 (2001) 181.
- [2] M. Niculescu, N. Vaszilcsin, M. Birzescu, P. Budrueac, E. Segal, J. Therm. Anal. Cal., 65 (2001) 881.
- [3] M. Niculescu, M. Birzescu, E. Şisu, P. Budrueac, Thermochim. Acta, 493 (2009) 1.
- [4] M. Niculescu, R. Dumitru, A. Magda, G. Bandur, E. Şisu, Rev. Chim. (Bucharest), 58 (2007) 932.
- [5] M. Birzescu, M. Niculescu, R. Dumitru, O. Carp, E. Segal, J. Therm. Anal. Cal. 96 (2009) 979.
- [6] M. Niculescu, R. Dumitru, A. Magda and V. Pode, Rev. Chim. (Bucharest), 64 (2013) 271.
- [7] M. Niculescu and P. Budrueac, Rev. Roum. Chim., 58 (2013) 381.
- [8] M. Niculescu, P. Budrueac, I. Ledeti, V. Pode and M. Birzescu, Rev. Roum. Chim., 58 (2013) 387.
- [9] M. Niculescu, D. Roşu, I. Ledeti, M. Milea and P. Budrueac, Rev. Roum. Chim., 58 (2013), 543.
- [10] M. Niculescu, N. Vaszilcsin, C.M. Davidescu, P. Negrea, M. Birzescu, P. Budrueac, Rev. Roum. Chim., 48 (2013), 997.
- [11] a) M. Stefanescu, V. Sasca, M. Birzescu, J. Therm. Anal. Cal., 72 (2003) 515.
b) M. Birzescu, Complex combinations with ethylene glycol and its oxidation products. Ph.D. Thesis, University of Bucharest, 1998.
- [12] M. Brezeanu, E. Safarica, E. Segal, L. Patron, T. Robu, Rev. Roum. Chim., 27 (1982) 137.

- [13] M. Brezeanu, E. Tatu, S. Bocai, O. Brezeanu, E. Segal, L. Patron, *Thermochim. Acta*, 78 (1984) 351.
- [14] J. Haenen, W. Visscher, E. Barendrecht, *J. Electroanal. Chem.* 208 (1986) 273.
- [15] D.P. Lapham, I. Colbeck, J. Schoonman, Y. Kamlag, *Thin Solid Films*, 391 (2001) 17.