Synthesis, Characterization and Voltammetric Studies of Trinuclear Mixed Valence Iron oxo Complexes $[Fe_2MO(OAc)_6(OH_2)_3]$, M (II)= Fe, Co, Cu

MARIA-GABRIELA ALEXANDRU[1]*, OLIVIER BURIEZ[2], IOANA JITARU[1]

[1]University "Politehnica" of Bucharest, Faculty of Applied Chemistry and Materials Science, Inorganic Chemistry Department, 1 Polizu, Bucharest, Romania

[2]UMR CNRS 8640 "PASTEUR" and LIA CNRS XiamENS "NanoBioChem", Ecole Normale Supérieure, Département de Chimie, Université Pierre et Marie Curie-Paris 6, 24 rue Lhomond, 75231 Paris cedex 05 (France)

*Three oxo iron compounds $[Fe_2MO(OAc)_6(OH_2)_3]\cdot S$, where M= Fe(II) (**1**), Co(II) (**2**), Cu(II) (**3**), Ac= $COCH_3$ and S= H_2O, CH_3OH were synthesized and characterized by mass spectrometry DEI and, DCI techniques and investigated by cyclic voltammetry in dimethylformamide (DMF). It is shown that each complex compound undergoes an electrochemical reduction of the iron(III) metal centers at around -1 V/SCE. The results obtained under these conditions support the existence of significant electronic interactions between homo- and heterometal centers, which may be finally influenced by the nature of the third metal (M).*

Keywords: oxo complex, iron, copper, cobalt, cyclic voltammetry.

Trinuclear oxo iron compounds have interesting structures considering the possibility of electron transfer between the metal centers and their magnetic and biological applications [1-3]. Oxo-centered iron compounds of $[Fe(III)_2MO(OAc)_6(OH_2)_3]^{0,+1}$ type, where M= Fe(II, III), Co(II), Ni(II), Cr(II) have been prepared since the beginning of the XXth century [4, 5] but their structures were established much later [6-9]. The configuration of mixed valence oxo iron carboxylates is similar to the active sites of various enzymes like hemosiderin, hemerythrin etc. [10-12]. Therefore, these biomimetic "basic acetates" are important for understanding some of these enzymatic processes. In particular, these specific enzyme activities are thought to rely on significant electronic interactions between the clustered metal centers. This is in agreement with the fact that the trinuclear oxo complex compounds exhibit interesting magnetic properties [13-17] as molecular magnets and catalytic activity, which cannot be accounted to one metal individually [18, 19].

The electronic interactions influence the redox properties of each metal center of the cluster and vary with their oxidation number. This should be readily analyzed by cyclic voltammetry [20, 21].

However, the study of these compounds is rather complicated in solution owing to rapid ligand-exchange reactions and low stability of the reduced forms [22–25]. To circumvent these limitations one may work with either a solvent or a ligand having stabilizing properties. For instance, R. Manchanda studied the electrochemical behaviour of oxo-centered trinuclear carboxylate-bridged iron complexes in pyridine as solvent to stabilize the $M_3(\mu_3$-O) trinuclear core [26]. Under these conditions, the electrochemical oxidation of $[Fe^{II}Fe^{III,III}_2(\mu_3\text{-}O)(OAc)_6(solv)_3]$ and $[Co^{II}Fe^{III,III}_2(\mu_3\text{-}O)(OAc)_6(solv)_3]$ and the reduction of $[Fe^{III,III,III}_3(\mu_3\text{-}O)(OAc)_6(solv)_3]$ were well defined mono-electronic reversible processes. On the other hand, it was studied the electron transfer in mixed-valence trinuclear oxo-centred iron complexes of the type $[Fe^{III}_2M^{II}OL_3]$ (M= Fe, Co, Ni, Cu) in which L is a pentadentate ligand designed to coordinate all three metal atoms in the central cluster and to inhibit dissociation and solvent exchange processes [27]. Under these conditions it was especially shown, in the case of the homonuclear complex $[Fe_3OL_3]$, that all four redox states from $[M^{III}_3OL_3]^+$ to $[M^{II}_3OL_3]^{2-}$ are electrochemically accessible.

This paper presents preliminary results obtained from the electrochemical activation of three synthesized mixed valence trinuclear oxo iron compounds $[Fe_3O(OAc)_6(OH_2)_3]\cdot 2H_2O$ (**1**), $[Fe_2CoO(OAc)_6(OH_2)_3]\cdot 2H_2O$ (**2**), and $[Fe_2CuO(OAc)_6(OH_2)_3]\cdot 2CH_3OH$ (**3**) in dimethylformamide (DMF) as solvent. This work performed under these conditions brought some further insight to both electronic interactions and reactivity of such complexes.

Experimental part

All reagents and solvents were purchased from Fluka® and used as received.

(**1**) was synthesized according to [28]. *Anal.* Calculated for Fe3C12H28O18 (%): C, 22.94; H, 4.46. Found: C, 22.74; H, 4.34.

(**2**) was prepared according to [28]. *Anal.* Calculated for Fe2CoC12H28O18 (%): C, 22.82; H, 4.44. Found: C, 22.52; H, 4.02.

(**3**) was obtained using an adapted method of [9]. A mixture of 2 mmoles $Fe(NO_3)_3\cdot 9H_2O$ and 4 mmoles $Cu(OAc)_2\cdot H_2O$ dissolved in 25 mL CH_3OH was heated at 70^{0}C with continuous stirring until dryness. The resulting solid was washed with a mixture of tetrahydrofurane:hexane= 3:1 and dried in air. *Anal.* Calculated for Fe2CuC14H32O18 (%): C, 25.33; H, 4.82. Found: C, 25.17; H, 4.55.

Elemental analyses were carried out by the "Service de Microanalyse" I.C.S.N.- C.N.R.S. Infrared spectra were recorded on a TENSOR 27 spectrometer in the 600-4000 cm^{-1} range. Mass spectra were recorded on a GCQ THERMOELECTRON apparatus. UV-Vis spectra were recorded on Jasco V-560 between 200-850 nm. Cyclic voltammetry experiments were performed at room temperature under argon atmosphere, in a three-electrode cell using an AUTOLAB potentiostat. A saturated calomel electrode (SCE – Tacussel) was used as the reference and was separated from the solution by a bridge compartment

* *Tel.: 0745755730*

filled with the same solvent/supporting electrolyte used in the cell. The counter electrode was an 1 cm gold wire (Goodfellow – 1mm diameter). A home-made glassy carbon working electrode (1 mm diameter - Goodfellow) was used. Tetrabutylammonium tetrafluoroborate ($TBABF_4$) used as the supporting electrolyte was prepared from $NaBF_4$ and *n*-$TBAHSO_4$, recrystallized from ethyl OAc-hexane and dried at 60°C.

Results and discussions

a) Infrared spectra

The peaks in the 400-750 cm^{-1} range belong to the stretching vibrations characteristic for M_3O core: ν_{asym}Fe-O at 563 cm^{-1}, 559 cm^{-1} for (**1**) and (**2**) at 663 cm^{-1} for (**3**); ν_{asym}Cu-O at 500 cm^{-1} and ν_{sym}Cu-O at 420 cm^{-1} for (**3**). Other important peaks are: 1539 cm^{-1} (**1**), 1581 cm^{-1} (**2**), 1580 cm^{-1} (**3**) for $\nu_{asym}COO^-$; 1413 cm^{-1} (**1**), 1409 cm^{-1} (**2**), 1416 cm^{-1} (**3**) for $\nu_{sym}COO^-$. Thus the carboxyl group exhibits bidentate bridging coordination mode. Specific signals for ν_{HOH} (coordinated water) can be observed at 3388 cm^{-1} (**1**), 3407 cm^{-1} (**2**) and at 3315 cm^{-1} for (**3**) [28].

b) Mass spectra

Oxo compounds have been analyzed by mass spectrometry techniques like FAB, ESI, EI [29, 30].

In this work the trinuclear mixed valence oxo compounds (**1**), (**2**) were characterized by mass spectrometry DEI+ (Desorption Electron Impact) method and (**3**) by DCI+ (Desorption Chemical Ionization) technique. The obtained mass spectrum of (**1**) is shown as example in figure 1 and the assignment of the peaks is presented in the tables 1, 2, 3 for (**1**), (**2**) and (**3**).

The fragmentation of (**2**) and (**3**) follows a different pattern in comparison with the oxo complex (**1**) since it lacked any $[Fe_2O]$ system as observed in the first two cases.

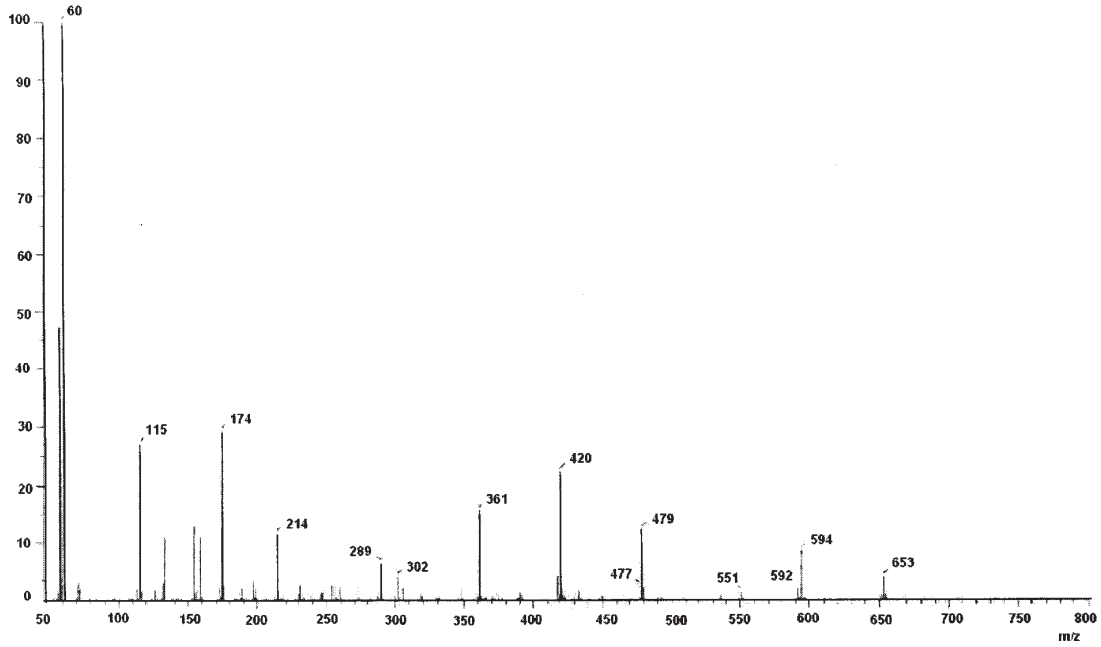

Fig. 1. Mass spectrum for (**1**)

Table 1

ASSIGNMENT OF THE PEAKS IN DEI+ MASS SPECTRUM FOR (**1**)

Observed peak (m/z)	Fragment assignment	Calculated mass of the fragment	Intensity (%)
60	$[H_2OAc]^+$	61	100
115	$Fe(OAc)^+$	114.85	28
174	$Fe(OAc)_2^+$	174.85	30
302	$[Fe_3O(OAc)_2]^+$	302.55	5
361	$[Fe_3O(OAc)_3]^+$	361.55	16
420	$[Fe_3O(OAc)_4]^+$	420.55	24
479	$[Fe_3O(OAc)_5]^+$	479.55	13
594	$[Fe_3O(OAc)_6(H_2O)_3]^+$	592.55	10

Table 2

ASSIGNMENT OF THE PEAKS IN DEI+ MASS SPECTRUM FOR (**2**)

Observed peak (m/z)	Fragment assignment	Calculated mass of the fragment	Intensity (%)
60	$[H_2OAc]^+$	60	14
115	$Fe(OAc)^+$	114.85	4
119	$Co(OAc)^+$	118	6
246	$[Fe_2O(OAc)_2]^+$	246.7	9
308	$[Fe_2O(OAc)_3]^+$	305.7	16
367	$[Fe_2O(OAc)_4]^+$	365.7	50
426	$[Fe_2CoO(OAc)_4]^+$	424.7	90
482	$[Fe_2CoO(OAc)_5]^+$	483.7	10
543	$[Fe_2CoO(OAc)_6]^+$	542.7	100
600	$[Fe_2CoO(OAc)_6(H_2O)_3]^+$	596.7	92

c) UV-Vis spectroscopy

The UV-Vis reflectance spectra of (**1**) and (**2**) (fig. 2) present bands characteristic for the absorption of $(OAc)^-$ ion in UV range, and *d-d* transitions specific for Fe(III) in octahedral symmetry [28].

The UV-Vis reflectance spectrum of (**3**) contains bands specific for Fe(III) $^4T_{2g}(G) \leftarrow {}^6A_{1g}$ at 530 nm and for Cu(II) at 670 nm $^2T_{2g} \leftarrow {}^2E_g$ which interfere very probable with $^4T_{1g} \leftarrow {}^6A_{1g}$ electronic transition for Fe(II) in octahedral symmetry from ~790 nm. The intervalence Fe(III)-Cu(II) charge transfer band appears at 407 nm and the absorption band of $(OAc)^-$ ligands at 244 nm [31].

*d) Stability study of trinuclear oxo-compounds (**1**), (**2**) and (**3**) in DMF solutions*

The stability of the oxo-trinuclear complex compounds (**1**), (**2**), (**3**) in DMF, the solvent used in cyclic voltammetry analysis, is essential to be determined for a correct judgment of the voltammetry experiments results. The UV-Vis spectra showed no difference regardless their periodicity. Several characteristic weak bands can be noticed between 400 and 500 nm for each compound. Their absorption maximum remained practically constant as a function of time showing their stability in DMF (fig. 2a, 2b, 2c).

Observed peak (m/z)	Fragment assignment	Calculated mass of the fragment	Intensity (%)
117	$Fe(OAc)^+$	114.85	100
127	$Cu(OAc)^+$	122.54	23
182	$[Cu(OAc)_2]^+$	182.54	7
245	$[Fe_2O(OAc)_2]^+$	246.7	14
303	$[Fe_2O(OAc)_3]^+$	305.7	32
363	$[Fe_2O(OAc)_4]^+$	364.7	7
426	$[Fe_2CuO(OAc)_4]^+$	428.24	6
486	$[Fe_2CuO(OAc)_5]^+$	487.24	5
549	$[Fe_2CuO(OAc)_6]^+$	546.24	6
667	$[Fe_2CuO(OAc)_6(H_2O)_3]^+ \cdot 2CH_3OH$	664.24	5

Table 3
ASSIGNMENT OF THE PEAKS IN DCI+ MASS SPECTRUM FOR (**3**)

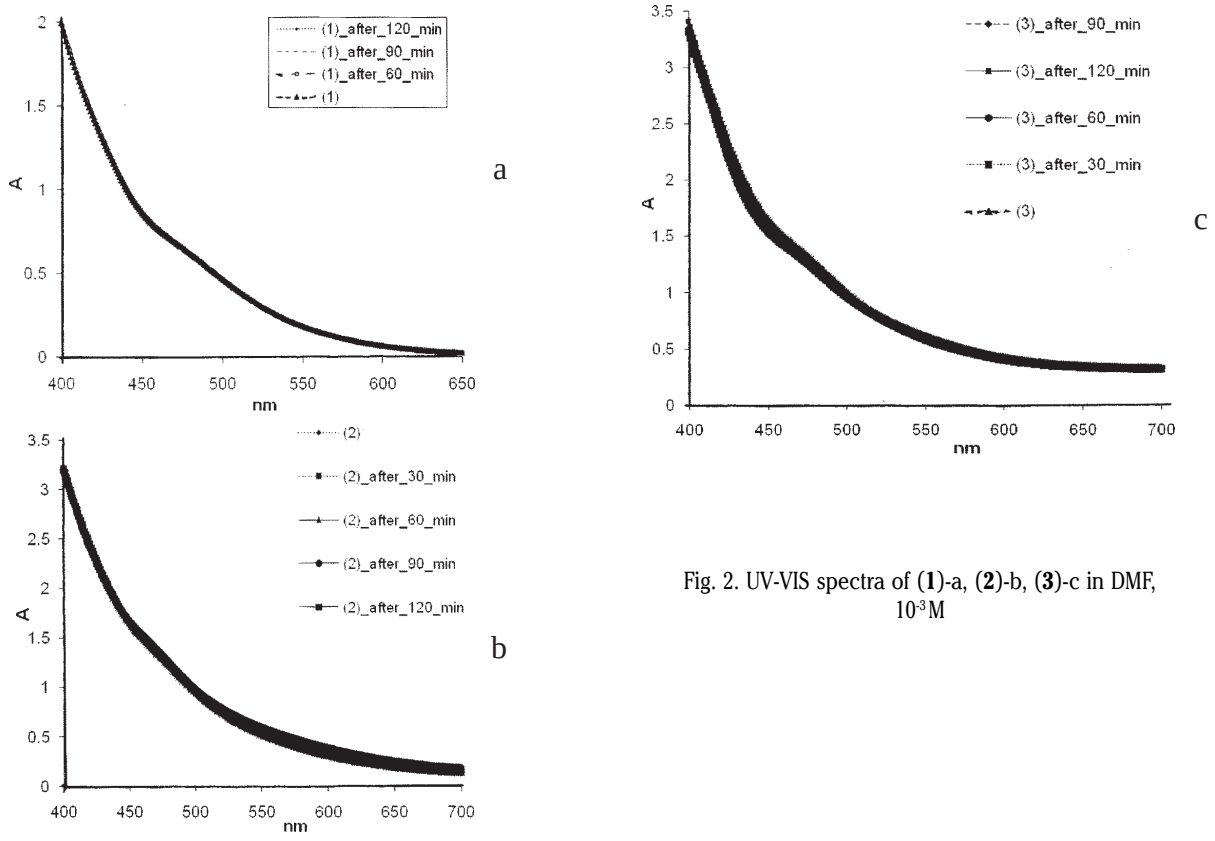

Fig. 2. UV-VIS spectra of (**1**)-a, (**2**)-b, (**3**)-c in DMF, 10^{-3}M

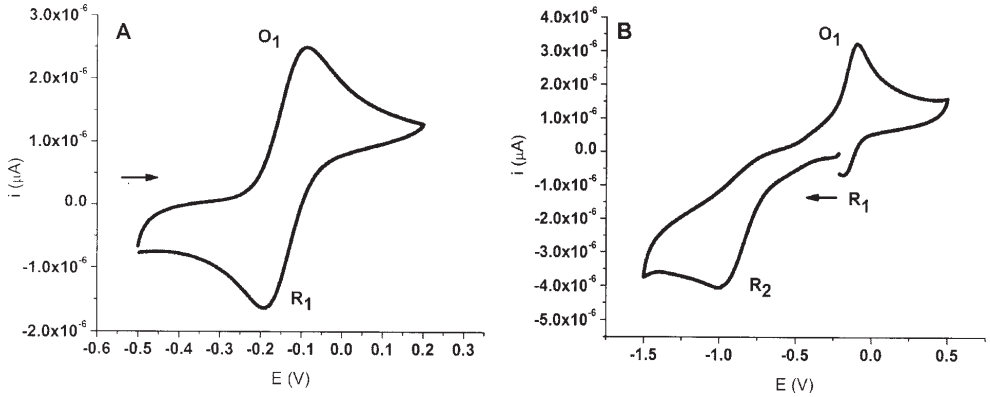

Fig. 3. Cyclic voltammograms of complex (**1**) (2 mM) in DMF + $TBABF_4$ (0.1 M) recorded at 0.2 V s^{-1} at a glassy carbon electrode (1 mm diameter). **A**: initial oxidative scan; **B**: initial reductive scan

e) Cyclic voltammetry

Complex (**1**)

The cyclic voltammogram displayed in figure 4**A** shows that compound (**1**) was oxidized in a reversible process, at E_{O1} = -0.1 V, demonstrating the stability of the electrogenerated cationic tri-iron(III) complex in DMF on the time-scale of cyclic voltammetry (fig. 3 A).

It was reported that the complex $[Fe_3^{III}O(O_2C_4H_5)_6(H_2O)_3]^+$ is chemically stable in DMF and could be electrochemically reduced, in a reversible wave, into the corresponding $[Fe^{II}Fe_2^{III}O(O_2C_4H_5)_6(H_2O)_3]$ compound. This behaviour supports the stability of both the reduced and the oxidized forms of the trinuclear iron complex in solvents which do not affect the structure of the complex (DMF, CH_3CN) [22].

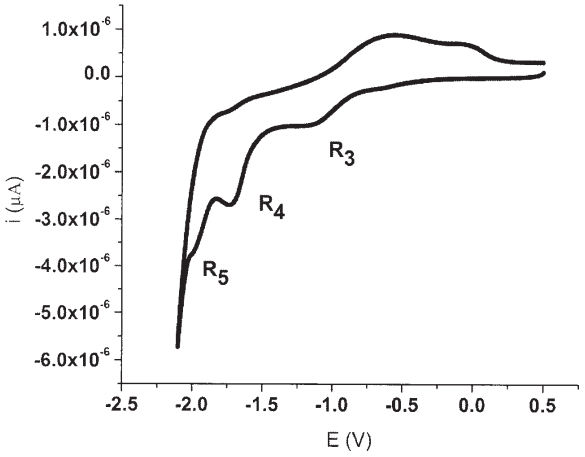

Fig. 4. Cyclic voltammograms of complex (**2**) (2 mM) in DMF + $TBABF_4$ (0.1 M) recorded at 0.2 V s^{-1} at a glassy carbon electrode (1 mm diameter)

O_1/R_1: $[Fe^{II}Fe_2^{III}O(OAc)_6(OH_2)_3] \rightleftharpoons [Fe_3^{III}O(OAc)_6(OH_2)_3]^+ + e$ (I)

R_2: $[Fe^{II}Fe_2^{III}O(OAc)_6(OH_2)_3] + 2e \longrightarrow [Fe_3^{II}O(OAc)_6(OH_2)_3]^{2-}$ (II)

Contrary to the oxidation process, the electrochemical reduction of complex (**1**), at E_{R2} = -1.0 V, produces an unstable species as attested by the chemical irreversibility of R_2 (fig. 3B). On the other hand, owing to the slow electron transfer rate involved in this reduction process, the peak intensity of R_2 can be considered as being approximately the double of that of wave O_1. As a consequence, the electrochemical process occurring at wave R_2 is very likely bi-electronic and involves the monoelectronic reduction of the two iron(III) metal centers.

Complex (**2**)

Replacement of the iron(II) redox center with a cobalt(II) one, leads to the complex reductive voltammogram shown in figure 4.

The first reduction wave R_3 was located at a slightly more negative potential value than wave R_2, observed for the reduction of the tri-iron complex, suggesting some electronic interactions between the cobalt and the iron metal centers. Nevertheless, the electron transfer rate is as slow as that observed previously for the reduction of (**1**). Moreover, the peak intensity of R_3 is similar to that of R_2. Accordingly, the wave R_3 very likely involves the mono-electronic reduction of the iron(III) metal centre into the corresponding iron(II). The peak at around -1.75 V (R_4) is assigned to the reduction of the iron center from the species formed after the first reduction process. Conversely, the third reduction wave, R_5, could be attributed to a product possessing a cobalt(II) redox center. This is very likely because under the same conditions (solvent, scan rate, electrode), the electrochemical reduction of $Co^{II}(OAc)_2$ occurred in the same electrochemical window (E= -1.90 V). Addition of increasing amounts of $Co^{II}(OAc)_2$ in a solution containing compound (**2**) led to an increase of the peak current of R_5 whereas the intensities of both R_3 and R_4 remained constant.

Finally the reduction of both the starting compound (**2**) and the various species produced after its decomposition, leads to the production of free $(OAc)^-$ ions. The reduction wave of the $(OAc)^-$ could be observed at -2.5 V and its assignment was confirmed by comparison with the cyclic voltammogram of NaOAc performed under the same conditions.

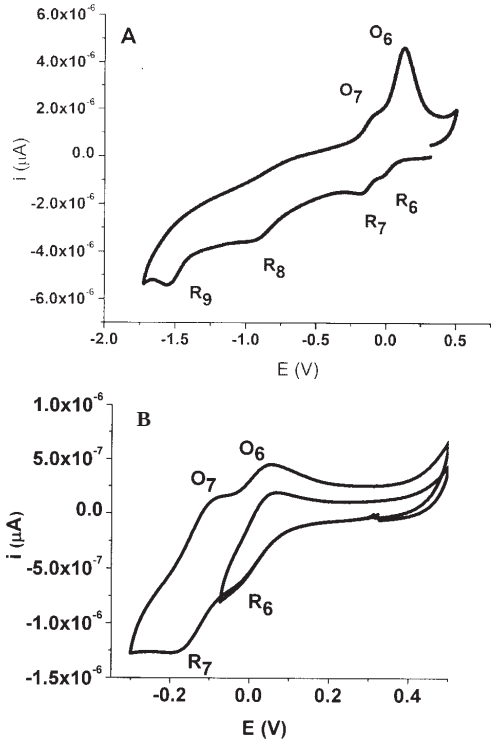

Fig. 5. Cyclic voltammograms of complex (3) (2 mM) in DMF + $TBABF_4$ (0.1 M) recorded at 0.2 V s^{-1} at a glassy carbon electrode (1 mm diameter) within two different electrochemical windows (**A** and **B**)

Complex (**3**)

By replacing the cobalt metal center with a copper one which was supposed to be reduced at a less negative potential value we obtained the reductive voltammograms of complex (**3**) displayed in figura 5A, 5B.

The cyclic voltammogram of the mixed Fe-Cu compound exhibited two new and less negative reversible reduction waves R_6 and R_7 located at E_{R6} = -0.04 V and E_{R7} = -0.17 V, respectively. By analogy with our previous results, these waves are certainly linked to the reduction of the copper redox center. However, the cyclic voltammogram of $Cu^{II}(OAc)_2$ exhibited a single irreversible wave at around -1.0 V. On the other hand, we can rule out a possible two successive mono-electronic reduction leading to the production of the Cu(I) and Cu(0) species in R_6 and R_7, respectively. When the potential scan was swept until more negative values, a new wave R_8 was exhibited at - 0.90 V resembling (localization, peak intensity, and electron transfer rate) to R_2, complex (**1**) and to R_3, complex (**2**). At -1.55 V occurs the reduction peak R_9 similar to R_4 observed previously for complex (**2**) and in consequence both R_8 and R_9 can be assigned to the reduction of the iron(III) metal centers. This demonstrates the stability of the newly formed complex after the reduction of the copper metal center.

The reduction wave of the $(OAc)^-$ could be observed at - 2.4 V.

Conclusions

The electrochemical behavior of three synthesized mixed valence trinuclear oxo iron compounds has been investigated in DMF, solvent in which the complex compounds were stable. The stability was proven using UV-Vis spectroscopy. The preliminary results obtained under these conditions support the existence of electronic interactions between homo- and heterometalic centers, which may be finally determined by the nature of the third metal.

References

1. ZHANG, K.-L., SHI, Y.- J., YOU, X.- Z., YU, K.- B., J. Mol. Struct., **743**, nr. 1-3, 2005, p. 73
2. VRUBEL, H., HASEGAWA, T., DE OLIVEIRA, E., NUNES, F. S., Inorg. Chem. Commun., **9**,2006, p. 208
3. KEENEY, L., HYNES, M. J., Dalton Trans., **8**, 2005, p. 1524
4. WEINLAND, R., GUSSMANN, E., Ber. Deut. Chemischen Ges. **42**, 1909, p. 2997
5. WEINLAND, R., HOLTMEIER, H., Z. Anorg. Chem., **173**, 1928, p. 49
6. BLAKE, A. B., YAVARI, A., HATFIELD, W., SETHULEKSHMI, C. N., J. Chem. Soc., Dalton Trans. **12**, 1985, p. 2509
7. SATO, T., AMBE, F., Acta Cryst., **C52**, 1996, p. 3005
8. OH, S. M., HENDRICKSON, D. N., HASSETT, K. L., DAVIS, R. E., J. Am. Chem. Soc., **107**, 1985, p. 8009
9. PRODIUS, D., TURTA, C., MEREACRE, V., SHOVA, S., GDANIEC, M., SIMONOV, Y., LIPKOWSKI, J., KUNCSER, V., FILOTI, G., CANESCHI, A., Polyhedron, **25**, 2006, p. 2175
10. LIPPARD, S. J., Angew. Chem. Int. Ed., **27**, 1988, p.344
11. ZHU, H., ALEXEEV, D., HUNTER, D. J. B., CAMPOPIANO, D. J., SADLER, P. J., Biochem J., **376**, 2003, p. 35
12. HOMES, M. A. J., STENKAMP, R. E., J. Mol. Biol., **220**, 1991, p.723
13. KURTZ, D. M. J., Chem. Rev., **90**, 1990, p. 585
14. RUMBERGER, E. M., HILL, S., EDWARDS, R. S., WERNSDORFER, W., ZAKHAROV, L. N., RHEINGOLD, A. L., CHRISTOU, G., HENDRICKSON, D. N., Polyhedron, 22, 2003, p. 1865
15. RAPTOPOULOU, C. P., SANAKIS, Y., BOUDALIS, A. K., PSYCHARIS, V., Polyhedron, **24**, 2005, p. 711
16. JANG, H. G., KAJI, K., SORAI, M., WITTEBORT, R. J., GEIB, S. J., RHEINGOLD, A. L., HENDRICKSON, D. N., Inorg. Chem., **29**, 1990, p. 3547
17. GAVRILENKO, K. S., VERTES, A., VANKO, G., KISS, L. F., ADDISON, A. W., WEYHERMÜLLER, T., PAVLISHCHUK, V. V., Eur J. Inorg. Chem., **12**, 2002, p. 3347
18. ITO, S., INOUE, K., MASTUMOTO, M., J. Am. Chem. Soc., **104**, 1982, p. 6450
19. KANAI, H., HAYASHI, H., KOIKE, T., OHSUGA, M., MATSUMOTO, M., Journal of Catalysis, **138**, 1992, 611
20. PUI, A., FISCHER, H., KOPF, H., REV. CHIM. **59**, 2008, p. 1317
21. NEMTOI, G., SECULA, M., CRETESCU, I., PETRESCU, S., Rev. Chim. (Bucharest) **58**, no. 12, 2007, p. 1216
22. SOWREY, F. E., MACDONALD, C. J., CANNON, R. D., J. Chem. Soc., Faraday Trans., **94**, 1998, p. 1571
23. STRAUGHAN, B. P., LAM, O. M., EARNSHAW, A. J., Chem. Soc., Dalton Trans. 97 (1987)
24. LOSADA, G., MENDIOLA, M. A., SEVILLA, M. T., Inorg. Chim. Acta., **255**, 1997, p. 125
25. BOND, M. A., CLARK, R. J. H., HUMPHREY, D. G., PANAYIOTOPOLOUS, P., SKELTON, B. W., WHITE, A. H., J. Chem. Soc., Dalton Trans., **12**, 1998, p. 1845
26. MANCHANDA, R., Inorganica Chimica Acta, **245**, 1996, p. 91
27. STADLER, C., DAUB, J., KOHLER, J., SAALFRANK, R. W., COROPCEANU, V., SCHUNEMANN, V., OBER, C., TRAUTWEIN, A. X., PARKER, S. F., POYRAZ, M., INOMATA, T., CANNON, R. D., J. Chem. Soc., Dalton Trans., **22**, 2001, p. 3373
28. ALEXANDRU, M.-G., JITARU, I., OPREA, O., ALEXANDRESCU, L., Rev. Chim. (Bucharest). **60**, no. 6, 2009, p. 592
29. PALII, S. P., RICHARDSON, D. E., HANSEN, M. L., IVERSEN, B. B., LARSEN, F. K., SINGEREAN, L., TIMCO, G. A., GERBELEU, N. V., JENNINGS, K. R., EYLER, J. R., Inorganica Chimica Acta, **319**, 2001, p. 23
30. BARANWAL, B. P., FATMA, T., J. Mol. Struct., **750**, 2005, p. 72
31. LEVER, A. (1984). Inorganic electronic spectroscopy, 2nd ed., Elsevier, Amsterdam

Manuscript received: 30.09.2009