Electrochemical Studies for Interaction between [Cu(salen)] and La(III) Ion in *N*,*N*-Dimethylformamide

Kazuhiro Manseki,*[†] Yuko Shimizu,[†] Akiko Obata,[††] Hiroshi Sakiyama,[†,††] Kei Unoura,[††]
Masatomi Sakamoto,*[†,††] Yuzo Nishida,[††] Yoshihiko Sadaoka,[†††] and Hisashi Ōkawa[††††]
[†]*Department of Human Sensing and Functional Sensor Engineering, Graduate School of Science and Engineering, Yamagata University, Kojirakawa-machi, Yamagata 990-8560*
[††]*Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Kojirakawa-machi, Yamagata 990-8560*
[†††]*Department of Materials Science and Engineering, Faculty of Engineering, Ehime University, Bunkyo-cho, Matsuyama 790-8577*
[††††]*Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581*

(Received August 27, 2001; CL-010837)

The interaction between [Cu(salen)] and La(III) in DMF was studied by cyclic voltammetry and EQCM (Electrochemical Quartz Crystal Microbalance) technique. The quasi-reversible redox wave of [Cu(salen)] around –1.1 V vs Ag/AgCl was replaced by a reduction wave around –0.9 V on forming a [Cu(salen)···La] complex. The CuLa complex disproportionated on the electrode to exhibit an anodic stripping of Cu(0) to Cu(II) around +0.2 V.

It is well known that d transition metal complexes of salen-like Schiff bases ($[M_a(SB)]$) act as 'complex ligands' toward a second d metal ion (M_b), providing dinuclear M_aM_b and trinuclear $M_aM_bM_a$ complexes bridged by the phenolic oxygen atoms of the SB ligands.[1] This synthetic principle was applied to 3d–4f mixed-metal systems in 1975,[2] and a fairly large amount of 3d–4f complexes were synthesized using [Cu(SB)] and [Ni(SB)] and investigated in their physicochemical properties in view of 3d–4f interaction.[3–10] On the other hand, the interaction between [M(SB)] and Ln(III) (Ln = lanthanide) in solution has been less studied so far, though an association of [Ni(SB)] and $Gd(fod)_3$ or $Gd(NO_3)_3$ in chloroform is evidenced by NMR spin–lattice relaxation studies.[11,12] We have shown that the fluorescence intensity of Eu(III) and Tb(III) is drastically diminished on forming [M(SB)···Ln] complex (M = Cu(II), Ni(II) or Cr(III)).[13–15] Here we report electrochemical studies for the [Cu(salen)]/La(III) system to demonstrate that Cu–La association gives rise to a distinct change in electrochemical behavior.

Cyclic voltammetric measurements were performed at 25 °C with an ALS-400 electrochemical analyzer. A three-electrode cell, which was equipped with a glassy carbon working electrode, an Ag/AgCl reference electrode, and a platinum coil auxiliary electrode, was used. EQCM measurements were carried out at 25 °C using the same ALS-400 electrochemical analyzer equipped with a quarz oscillator with 8-MHz resonance frequency as the working electrode on which Au was vapor-deposited. Tetrabutylammonium tetrafluoroborate was used as the supporting electrolyte.

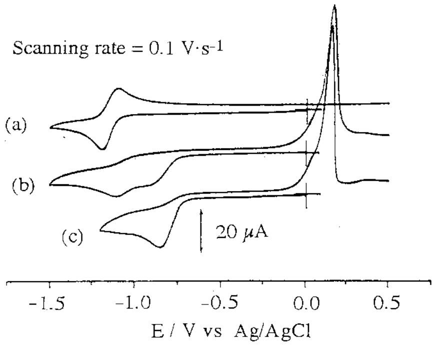

Figure 1. Effect of addition of $La(NO_3)_3·6H_2O$ on cyclic voltammogram of [Cu(salen)] (1×10^{-3} mol·dm^{-3}) in DMF: $[La(NO_3)_3·6H_2O]$ = (a) 0 mol·dm^{-3}; (b) 1×10^{-3} mol·dm^{-3}; (c) 1×10^{-2} mol·dm^{-3}.

[Cu(salen)] in DMF shows a quasi-reversible couple due to the Cu(II)/Cu(I) process around –1.1 V vs Ag/AgCl (Figure 1(a)). In order to see an effect of La(III) ion upon the electrochemical nature of [Cu(salen)], a DMF solution containing [Cu(salen)] and La(III) ion was prepared as follows. To a DMF solution of [Cu(salen)] were added 25–250 mm^3 of a methanolic solution (0.4 mol·dm^{-3}) of $La(NO_3)_3·6H_2O$ and the total volume of the solution was adjusted to 10 cm^3 with DMF. The concentration of [Cu(salen)] of the resulting solution was 1×10^{-3} mol·dm^{-3} and that of [La(III)] was 1×10^{-3}–1×10^{-2} mol·dm^{-3}. We have confirmed from the blank check that the presence of such a small amount of methanol (25–250 mm^3) has no effect upon the CV of [Cu(salen)] in DMF. When one equivalent of La(III) was added to a DMF solution of [Cu(salen)] (Figure 1(b)), the quasi-reversible couple around –1.1 V became irreversible and an irreversible reduction wave appeared near at –0.9 V. When ten equivalents of La(III) was added (Figure 1(c)), the original wave around –1.1 V virtually disappeared and the reduction wave near –0.9 V became more intense. The difference between the peak potentials of these two reduction waves is 0.2 V or more. This fact means that [Cu(salen)] and La(III) are equilibrated in DMF and the reduction wave around –0.9 V is associated with the Cu(II) of the [Cu(salen)···La] complex. It is known that the Cu(II)/Cu(I) couple of dinuclear CuM complexes (M = Pb(II), Mn(II), Fe(II), Co(II), Ni(II), Zn(II)) of diphenolate-based dinucleating ligand possessing a salen moiety shifts to a more positive potential because of the existence of the second metal (M) ion.[16] We have noticed that the CV for the [Cu(salen)]/[La] = 1/1 system (Figure 1(b)) changes with the scanning rate. In general the reduction peak around –0.9 V becomes weaker and the peak around –1.1 V becomes stronger with increasing the scanning rate up to 10 V·s^{-1}. This is understandable by taking into consideration the equilibrium, [Cu(salen)] + La(III) $\rightleftarrows$ [Cu(salen)···La]. That is, the amount of [Cu(salen)···La] in the diffusion layer must be reduced in the fast scanning if the equilibration is slow.

Another noticeable feature in Figure 1 is an oxidation peak appearing around +0.2 V in the presence of La(III). In order to gain an insight into this oxidation peak, simultaneous CV and EQCM (Electrochemical Quartz Crystal Microbalance) measurements were made using an Au working electrode (Figure 2). The CV patterns obtained on Au working electrode are essentially the same as those obtained on the glassy carbon working electrode in Figure 1. In the absence of La(III) the resonance frequency of the quartz oscillator shows a small minimum in the reduction process and a slight gradual increase in the reoxidation process (Figure 2(a)). The minimum corresponds to the reduction potential of [Cu(salen)]. Such small change in resonance frequency arises from some alteration in viscosity or composition near the electrode surface during the redox reaction.[17] In the presence of La(III), on the other hand, a large decrease of resonance frequency was observed in the reduction process and a large increase in the reoxidation process (Figure 2(b)). This means that the electrode weight increases on reduction and decreases on reoxidation. The EQCM result strongly suggests that the Cu(I)La(III) species produced on the electrode disproportionates into Cu(0) and Cu(II) (= [Cu(salen)]) and the resulting Cu(0) is deposited on the electrode but stripped when oxidized to Cu(II).

From above discussion the association of [Cu(salen)] and La(III) ion has been clearly evidenced by the electrochemical methods. Furthermore, this work illustrates that the EQCM method is effective to study electrochemical reaction involving anomalous adsorption/desorption process.

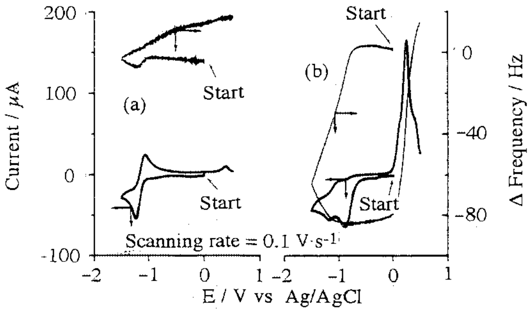

Figure 2. Simultaneous measurements of cyclic voltammogram and EQCM for [Cu(salen)] (1×10^{-3} mol·dm^{-3}) in DMF: [$La(NO_3)_3 \cdot 6H_2O$] = (a) 0 mol·dm^{-3}; (b) 2×10^{-3} mol·dm^{-3}.

This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan and JSPS Research Fellowships for Young Scientists.

References

1 E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 423 (1969).
2 G. Condorelli, I. Fragala, S. Giuffrida, and A. Cassol, *Z. Anorg. Allg. Chem.*, **412**, 251 (1975).
3 A. Seminara, S. Giuffrida, A. Musumeci, and I. Fragala, *Inorg. Chim. Acta*, **95**, 201 (1984)
4 A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei, and D. Gatteschi, *J. Am. Chem. Soc.*, **107**, 8128 (1985).
5 A. Bencini, C. Benelli, A. Caneschi, A. Dei, and D. Gatteschi, *Inorg. Chem.*, **25**, 572 (1986).
6 I. Ramade, O. Kahn, Y. Jeannin, and F. Robert, *Inorg. Chem.*, **36**, 930 (1997).
7 M. Sasaki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, Y. Sadaoka, M. Ohba, and H. Ōkawa, *Chem. Lett.*, **1998**, 911.
8 A. Gleizes, M. Julve, N. Kuzmina, A. Alikhanyan, F. Lloret, I. Malkerova, J. L. Sanz, and F. Senocq, *Eur. J. Inorg. Chem.*, **1998**, 1169.
9 J.-P. Costes, F. Dahan, A. Dupuis, and J.-P. Laurent, *New J. Chem.*, **1998**, 1525.
10 M. Sasaki, K. Manseki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, M. Sakai, Y. Sadaoka, M. Ohba, and H. Ōkawa, *J. Chem. Soc., Dalton Trans.*, **2000**, 259.
11 J. Y. Lee, D. A. Hanna, and G. W. Everett, Jr., *Inorg. Chem.*, **20**, 2004 (1981).
12 G. W. Everett, Jr., D. A. Hanna, and J. Y. Lee, *Inorg. Chim. Acta*, **64**, L15 (1981).
13 M. Sakamoto, M. Hashimura, K. Matsuki, A. Matsumoto, and H. Ōkawa, *Chem. Lett.*, **1991**, 1007.
14 M. Sakamoto, K. Yamamoto, M. Osaki, A. Matsumoto, and H. Ōkawa, *J. Alloys Compd.*, **192**, 42 (1993).
15 M. Sakamoto, K. Yamamoto, A. Matsumoto, Y. Nishida, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **67**, 2707 (1994).
16 H. Ōkawa, J. Nishio, M. Ohba, M. Tadokoro, N. Matsumoto, M. Koikawa, S. Kida, and D. E. Fenton, *Inorg. Chem.*, **32**, 2949 (1993).
17 D. A. Buttry and M. D. Ward, *Chem. Rev.*, **92**, 1355 (1992).